

THE D-AND F-BLOCK ELEMENTS

GENERAL PROPERTIES OF THE TRANSITION ELEMENTS (d-Block)

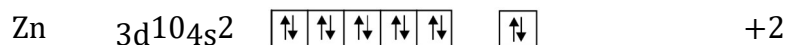
❖ **CHARACTERISTIC PROPERTIES OF TRANSITION ELEMENTS:**

- | | |
|------------------------------|---|
| (a) Variable oxidation state | (b) Coloured ions |
| (c) Paramagnetic properties | (d) Catalytic properties |
| (e) Formation of alloys | (f) Formation of interstitial compounds |
| (g) Formation of complexes. | |

Variable Valency or Variable Oxidation States

- (a) They exhibit variable valency due to involvement of (ns) and (n-1) d-electrons. Due to less energy difference between these electrons.
- (b) The oxidation states of all transition elements of '3d' series are as follows –

| Element | Conf. | Outer electronic configuration | | Oxidation states | | | | | | |
|---------|----------------------------------|--|--------------------------|------------------|----|----|----|----|----|--|
| Sc | 3d ¹ 4s ² | <div><div>↑</div><div></div><div></div><div></div><div></div></div> | <div><div>↑↓</div></div> | | +3 | | | | | |
| | | 3d | 4s | | | | | | | |
| Ti | 3d ² 4s ² | <div><div>↑</div><div>↑</div><div></div><div></div><div></div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | | | | |
| V | 3d ³ 4s ² | <div><div>↑</div><div>↑</div><div>↑</div><div></div><div></div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | +5 | | | |
| Cr | 3d ⁵ 4s ¹ | <div><div>↑</div><div>↑</div><div>↑</div><div>↑</div><div>↑</div></div> | <div><div>↑</div></div> | +1 | +2 | +3 | +4 | +5 | +6 | |
| Mn | 3d ⁵ 4s ² | <div><div>↑</div><div>↑</div><div>↑</div><div>↑</div><div>↑</div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | +5 | +6 | +7 | |
| Fe | 3d ⁶ 4s ² | <div><div>↑↓</div><div>↑</div><div>↑</div><div>↑</div><div>↑</div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | +6 | | | |
| Co | 3d ⁷ 4s ² | <div><div>↑↓</div><div>↑↓</div><div>↑</div><div>↑</div><div>↑</div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | | | | |
| Ni | 3d ⁸ 4s ² | <div><div>↑↓</div><div>↑↓</div><div>↑↓</div><div>↑</div><div>↑</div></div> | <div><div>↑↓</div></div> | +2 | +3 | +4 | | | | |
| Cu | 3d ¹⁰ 4s ¹ | <div><div>↑↓</div><div>↑↓</div><div>↑↓</div><div>↑↓</div><div>↑↓</div></div> | <div><div>↑</div></div> | +1 | +2 | | | | | |



(c) Highest oxidation state of transition elements can be calculated by $n + 2$ where (n = number of unpaired electrons) It is not applied for Cr and Cu.

(d) The transition metal ions having stable configuration like d^0 d^5 or d^{10} are more stable.

Ex. Sc^{+3} , Ti^{+4} , V^{+5} , Fe^{+3} , Mn^{+2} , Zn^{+2} etc.

(e) In aqueous medium Cr^{+3} is stable.

(f) Co^{+3} and Ni^{+2} is stable in complexes.

(g) In aqueous medium due to disproportionation Cu^{+1} is less stable than Cu^{+2} while its configuration is $3d^{10}$

(h) Most common oxidation state among the transition elements is +2.

(i) Highest oxidation state shown by transition elements of '4d' and '5d' series is +8 by Ru (44) and Os (76).

(j) The common oxidation state shown by elements of IIIB i.e., Sc, Y, La and Ac is +3 as their divalent compounds are highly unstable.

(k) In lower oxidation state transition elements form ionic compounds and in higher oxidation state their compounds are covalent.

(l) They also shows zero oxidation state in their carbonyl compounds like $\text{Ni}(\text{CO})_4$.

(m) Usually transition metal ions in their lower oxidation state act as reducing agents and in higher oxidation state they are oxidising agents.

Ex. Sc^{+2} , Ti^{+2} , V^{+2} , Fe^{+2} , Co^{+2} etc are reducing agents

Cr^{+6} , Mn^{+7} , Mn^{+6} , Mn^{+5} , Mn^{+4} etc are oxidising agents.

Standard Electrode Potentials

The ionization enthalpy magnitude indicates the energy needed to remove electrons and create a specific oxidation state of the metal in a compound. Consequently, ionization enthalpy values provide insights into the thermodynamic stability of

transition metal compounds in various oxidation states. A lower ionization enthalpy for the metal implies greater stability for its compound

For example, the first four ionisation enthalpies of nickel and platinum are given below:

| Ionisation enthalpies | Ni | Pt |
|-----------------------|---|--|
| $IE^1 + IE^2$ | $2.49 \times 10^3 \text{ KJ mol}^{-1}$ | $2.66 \times 10^3 \text{ KJ mol}^{-1}$ |
| $IE^3 + IE^4$ | $8.8 \times 10^3 \text{ KJ mol}^{-1}$ | $6.70 \times 10^3 \text{ KJ mol}^{-1}$ |
| Total | $11.29 \times 10^3 \text{ KJ mol}^{-1}$ | $9.36 \times 10^3 \text{ KJ mol}^{-1}$ |

It is clear from the above table that the sum of first two ionization enthalpies is less for nickel than for platinum.



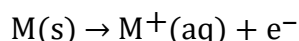
Consequently, the ionization of nickel to Ni^{2+} is more energetically advantageous in comparison to platinum. This establishes that nickel (II) compounds exhibit greater thermodynamic stability than platinum (II) compounds. Conversely, the total of the first four ionization enthalpies is lower for platinum than for nickel, as demonstrated by:



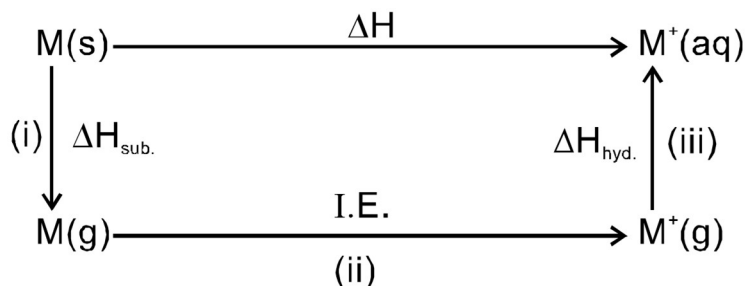
Hence, platinum (IV) compounds exhibit comparatively higher stability than nickel (IV) compounds. Consequently, K_2PtCl_6 , which features Pt (IV), is a recognized compound, while the corresponding nickel compound remains unknown. However, in solutions, the stability of these compounds is contingent upon electrode potentials.

Electrode potentials:

In addition to ionization enthalpy, factors like enthalpy of sublimation, hydration enthalpy, and ionization enthalpy collectively contribute to the stability of a specific oxidation state in a solution. This can be elucidated based on their electrode potential values. The oxidation potential of a metal encompasses the following process:



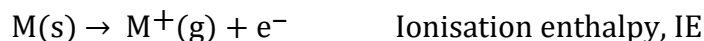
This process actually takes place in the following three steps as given in following flowchart:



- (i) In the first step, the atoms get isolated from one another and become independent in the gaseous state. This converts solid metal to the gaseous state. The energy needed for this step is known as enthalpy of sublimation.



- (ii) In the second step, the outer electron is removed from the isolated atom. The energy required for this change is ionisation enthalpy.



- (iii) In the third step the gaseous ion gets hydrated. In this process, energy known as hydration enthalpy, is liberated.



The oxidation potential which gives the tendency of the overall change to occur, depends upon the net effect of these three steps. The overall energy change is

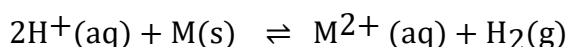
$$\Delta H = \Delta_{\text{sub}}H^\ominus + \text{IE} + \Delta_{\text{hyd}}H$$

Hence, ΔH represents the enthalpy change necessary to transform the solid metal, M, into the monovalent ion in an aqueous medium, $\text{M}^+(\text{aq})$. A similar cycle can be constructed for the formation of an anion in a solution, with the ionization enthalpy potentially replaced by electron gain enthalpy as the gaseous atom transforms into a gaseous anion. ΔH aids in predicting the stability of a specific oxidation state.

The smaller the values of total energy change for a given oxidation state in an aqueous solution, the greater the stability of that oxidation state. Electrode potentials serve as a measure of total energy change. Qualitatively, the stability of transition metal ions

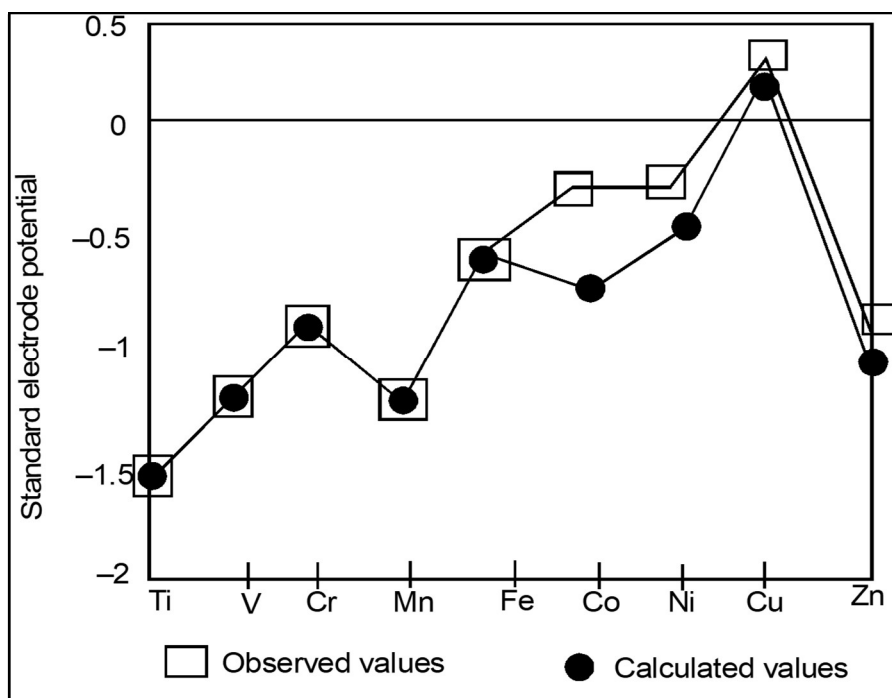
in various oxidation states can be assessed based on electrode potential data. The lower the electrode potential, or the more negative the standard reduction potential of the electrode, the more stable the oxidation state of the transition metal in the aqueous solution.

The electrode potentials of different metals can also be measured by forming the cell with standard hydrogen electrode. For the measurement of electrode potential of $M^{2+} | 1M$, the e.m.f. of the cell in which the following reaction occurs is measured:



Knowing the potential of $2H^+(aq) | H_2(g)$, it is possible to determine the potential of $M^{2+}(aq) | M$. For the first transition series, the E^\ominus values of $M^{2+}(aq) | M$ are given below:

The observed values of E^\ominus and those calculated using the data are compared in the following figure.



Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode potentials for the Reduction of M^{II} to M

| Element (M) | $\Delta_a H_q$ (M) | $\Delta_f H_1^\theta$ | $\Delta_f H_2^\theta$ | $\Delta_{\text{hyd}} H^\theta (M^{2+})$ | E^θ / V |
|-------------|--------------------|-----------------------|-----------------------|---|----------------|
| Ti | 469 | 661 | 1310 | -1866 | -1.63 |
| V | 515 | 648 | 1370 | -1895 | -1.18 |
| Cr | 398 | 653 | 1590 | -1925 | -0.90 |
| Mn | 279 | 716 | 1510 | -1862 | -1.18 |
| Fe | 418 | 762 | 1560 | -1998 | -0.44 |
| Co | 427 | 757 | 1640 | -2079 | -0.28 |
| Ni | 431 | 736 | 1750 | -2121 | -0.25 |
| Cu | 339 | 745 | 1960 | -2121 | 0.34 |
| Zn | 130 | 908 | 1730 | -2059 | -0.76 |

The results lead to the following conclusions:

- (i) There is no regular trend in these values. This is attributed to the irregular variation of ionisation enthalpies ($IE_1 + IE_2$) and the sublimation energies in the period.
- (ii) It may be noted that the electrode potentials of transition metals are low in comparison to elements of group 2 (e.g., $Ca = -2.87 V$). Compared to group 2 elements, the transition elements have fairly large ionisation enthalpies and very large enthalpies of atomization. These reduce their electrode potentials though their hydration enthalpies are large.
- (iii) Zinc has low enthalpy of atomization and fairly large hydration energy. But it has also low electrode potential ($-0.76 V$) because of its very high ionisation enthalpy ($IE_1 + IE_2$).
- (iv) It is clear from above table and figure that copper has positive reduction potential, E^θ ($0.34 V$) and this shows that copper is least reactive metal out of the first transition series. This unique behavior (+ve) E value of copper) also accounts for its inability to liberate H_2 from acids. It has been observed that only oxidizing acids (such as nitric acid and hot concentrated sulphuric acid) react with copper in which the acids are reduced. The high energy required to convert $Cu(s)$ to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.
- (v) In general, the value becomes, less negative across the series. This is related to the general increase in the sum of first and second ionisation enthalpies. It is interesting to note that the values of E^θ of Mn, Ni and Zn are more negative than expected from

the general trend. The relatively more negative values of E^\ominus for Mn and Zn are due to stability of half-filled d-sub-shell in Mn^{2+} ($3d^5$) and the completely filled ($3d^{10}$) configuration in Zn^{2+} . The exceptionally high E^\ominus value of Ni from regular trend is related to the highest negative enthalpy of hydration of Ni^{2+} ion.

Trends in the $\text{M}^{3+} | \text{M}^{2+}$ Standard Electrode Potentials

Except copper and zinc, all other elements of first transition series show +3 oxidation states also to form M^{3+} ions in aqueous solutions. The standard reduction potentials for $\text{M}^{3+} | \text{M}^{2+}$ redox couple are given below:

| | Ti | V | Cr | Mn | Fe | Co |
|--|-------|-------|-------|-------|-------|-------|
| $E^\ominus (\text{M}^{3+}(\text{aq}) \text{M}^{2+}(\text{aq}))$ (in Volt) | -0.37 | -0.26 | -0.41 | +1.57 | +0.77 | +1.97 |

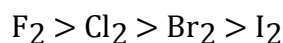
These values reveal the following facts:

- (i) The low value of scandium reflects the stability of Sc^{3+} which has a noble gas configuration.
- (ii) The comparatively high value for Mn shows that Mn^{2+} (d^5 configuration) is particularly stable. On the other hand, comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5 configuration).
- (iii) The comparatively low value of V is related to the stability of V^{2+} (due to half-filled t_{2g}^3 energy level of 3d orbitals in octahedral crystal field splitting).
- (iv) The E^\ominus value for $\text{Mn}^{3+} / \text{Mn}^{2+}$ couple much more positive than for $\text{Cr}^{3+} / \text{Cr}^{2+}$ or $\text{Fe}^{3+} / \text{Fe}^{2+}$. This is because of the much larger IIIrd ionisation energy of Mn (removal of electron from d^5 configuration).

Trends in Stability of Higher Oxidation States

Data on standard electrode potentials offer valuable insights into the stability of various oxidation states exhibited by an element. The highest oxidation states are typically observed in halides and oxides.

1. **In metal halides.** The transition elements undergo reactions with halogens at elevated temperatures, resulting in the formation of transition metal halides. These reactions exhibit substantial heat of reaction. However, once the reaction initiates, the generated heat is adequate to sustain the reaction. The halogens engage in the reaction in the following descending order



Halides of first transition series

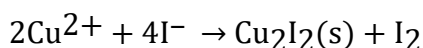
| Oxidation Number | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|--|------------------|------------------|------------------------------|------------------|------------------|-------------------------------|------------------|------------------|-------------------------------|------------------|
| +6 | | | | CrF ₆ | | | | | | |
| +5 | | | VF ₅ | CrF ₅ | | | | | | |
| +4 | | TiX ₄ | VX ₄ ^a | CrF ₄ | MnF ₄ | | | | | |
| +3 | ScX ₃ | TiX ₃ | VX ₃ | CrF ₃ | MnF ₃ | FeX ₃ ^a | CoF ₃ | | | |
| +2 | | TiX ₂ | VX ₂ ^c | CrF ₂ | MnX ₂ | FeX ₂ | CoF ₂ | NiX ₂ | CuX ₂ ^b | ZnX ₂ |
| +1 | | | | | | | | | CuX ^c | |
| where X = F, Cl, Br, I, X ^a = F, Cl, Br, X ^b = F, Cl, X ^c = Cl, Br, I | | | | | | | | | | |

Among the transition groups 3-12, variations in the stability of different oxidation states exist. Typically, the second and third transition series elements demonstrate higher coordination numbers, making their higher oxidation states more stable compared to the corresponding elements in the first transition series.

The following trends are observed from table regarding transition metal halides:

- In general, the elements of first transition series tend to exist in low oxidation states. Chromium to zinc form stable difluorides and the other chlorides are also known.
- Since fluorine is the most electronegative element, the transition metals show highest oxidation states with fluorine. The highest oxidation states are found in TiX₄ (tetrahalides, X = F, Cl, Br and I), VF₅ and CrF₆.
- The +7-oxidation state for Mn is not shown by simple halides. However, MnO₃F is known in which the oxidation state of Mn is +7.

- (iv) After Mn, the tendency to show higher oxidation states with halogens are uncommon. Iron and cobalt form trihalides FeX_3 ($\text{X} = \text{F}, \text{Cl}$ or Br) and CoF_3 .
- (v) The tendency of fluorine to stabilize the highest oxidation state is due to either higher lattice enthalpy as in case of CoF_3 or higher bond enthalpy due to higher covalent bonds e.g., VF_5 and CrF_6 .
- (vi) V(V) is shown by VF_5 only. However, the other halides undergo hydrolysis to form oxyhalides, VOX_3 .
- (vii) Fluorides are relatively unstable in their low oxidation states. For example, vanadium form only VX_2 ($\text{X} = \text{Cl}, \text{Br}$ or I) and copper can form CuX ($\text{X} = \text{Cl}, \text{I}$). All copper (II) halides are known except the iodide. This is because, Cu^{2+} oxidizes I^- to I_2 .



It has been observed that many copper (I) compounds are unstable in aqueous solution and they undergo disproportionation to Cu(II) and Cu(0) as :



Copper in +2 oxidation state is more stable than in +1 oxidation state. This can be explained on the basis of much larger negative hydration enthalpy ($\Delta_{\text{hyd}}H^\ominus$) of Cu^{2+} (aq) than Cu^+ , which is much more than compensates for the large energy required to remove the second electron i.e., second ionisation enthalpy of copper.

2. In metal oxides and oxo cations.

| Oxidation Number | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn |
|------------------|----|----------------|------------------------|----------------|-------------------------|-------------------------|----|----|----|----|
| +7 | | | | | Mn_2O_7 | | | | | |
| +6 | | | | CrO_3 | | | | | | |
| +5 | | | V_2O_5 | | | | | | | |
| +4 | | TiO_2 | V_2O_4 | CrO_2 | MnO_2 | Fe_2O_3 | | | | |

| | | | | | | | | | | |
|--------------|--------------------------------|------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|-----|-----|-----|
| +3 | Sc ₂ O ₃ | TiO ₃ | V ₂ O ₃ | Cr ₂ O ₃ | Mn ₂ O ₃ | FeO | CoO | NiO | CuO | ZnO |
| +2 | | TiO | VO | (CrO) | MnO | | | | CuO | |
| +1 | | | | | | | | | | |
| Mixed oxides | | | | | Mn ₃ O ₄ | Fe ₃ O ₄ | Co ₃ O ₄ | | | |

Oxygen's capacity to stabilize the highest oxidation state is evident in its oxides. The highest oxidation states in these oxides correspond to the group number.

For instance, scandium in group 3 exhibits a highest oxidation state of +3 in its oxides, Sc₂O₃, while manganese in group 7 shows +7 in Mn₂O₇. However, beyond group 7, no higher oxides of iron above Fe₂O₃ are known. Although higher oxidation states, such as +6, are seen in ferrates like FeO₄²⁻ in alkaline medium, they readily decompose to Fe₂O₃ and O₂. In addition to oxides, the oxidation of metals also stabilizes higher oxidation states, as seen in V^V as VO₂⁺, V^{IV} as VO²⁺, and Ti^{IV} as TiO²⁺. Notably, oxygen's ability to stabilize these high oxidation states surpasses that of fluorine.

For instance, manganese forms its highest fluoride as MnF₄, while its highest oxide is Mn₂O₇. This is attributed to oxygen's superior ability to form multiple bonds to metals. In covalent oxides like Mn₂O₇, each Mn is tetrahedrally surrounded by oxygen atoms, forming Mn–O–Mn bridges. Tetrahedral [MO₄]ⁿ⁻ ions are also known for vanadium (V), chromium (VI), manganese (VI), and manganese (VII).

Transition elements in the +2 and +3 oxidation states predominantly form ionic bonds, while with higher oxidation states, the bonds become essentially covalent. For instance, in MnO₄⁻, all bonds are covalent. As the oxidation number of a metal increases, the ionic character of their oxides decreases. Mn₂O₇, for example, is a covalent green oil. In these higher oxides, the acidic character is predominant. Thus, CrO₃ yields H₂CrO₄ and H₂Cr₂O₇, and Mn₂O₇ yields HMnO₄. V₂O₅ is amphoteric, mainly acidic, and reacts with alkalis to give VO₄³⁻ and with acids to produce VO₂⁺.

The relative stability of various oxidation states

- (a) The relative stabilities of various oxidation states of 3d-series element can be correlated with the extra stability of $3d^0, 3d^5$ & $3d^{10}$ configuration to some extent.

Ex. Stability of $Ti^{4+} (3d^0) > Ti^{3+} (3d^1) > Mn^{2+} (3d^5) > Mn^{3+} (3d^4)$

- (b) The higher oxidation state of 4d and 5d series element are generally more stable than the elements of 3d series.

Ex. (i) (oxidation state of Mo is +6), (4d series) & (5d series) are more stable due to their maximum oxidation state.

(ii) & (3d-series) are strong oxidizing agents.

- (c) Strongly reducing states probably do not form fluorides or oxides, but may well form the heavier halides. Conversely, strong oxidizing state form oxides & fluoride, but not Bromide and Iodide.

Ex.

- (i) V (Vanadium) react with halogens to form VF_5, VCl_5, VBr_3 , but doesn't form VBr_5 or VI_5 because in +5 oxidation state Vanadium is strong oxidizing agent thus convert Br^- & I^- to Br_2 & I_2 respectively, So VBr_3 & VI_3 are formed but not VBr_5 & VI_5 .

- (ii) On the other hand, VF_5 is formed because V^{5+} ion unable to oxidize highly electronegative & small anion F^-

- (iii) Similarly, highly electronegative and small O^{2-} ion formed oxides

Ex. VO_4^{3-}, CrO_4^{2-} & MnO_4^- etc.

Different oxidation state of chloride & oxides compound

| +2 | +3 | +4 | +5 | +6 | +7 |
|----------------|----------------------------|--|----------|----|----|
| $TiCl_2$ | $TiCl_3$ | $TiCl_4$ | | | |
| VCl_2 | VCl_3 | VCl_4 | $VOCl_3$ | | |
| (Ionic, basic) | Less ionic (Amphoteric) | Covalent and Acidic (Strong lewis acid) | | | |

| | | | | |
|-----|--------------|--------------------------------|------------------|---|
| (d) | TiO | Ti ₂ O ₃ | TiO ₂ | |
| | VO | V ₂ O ₃ | | V ₂ O ₅ |
| | CrO | Cr ₂ O ₃ | | CrO ₃ |
| | MnO | Mn ₂ O ₃ | MnO ₂ | MnO ₃ Mn ₂ O ₇ |
| | | | | |
| | Ionic, basic | Less Ionic (Amphoteric) | | Acidic, covalent |

Such compounds are expected to be unstable except in case where vacant d-orbitals are used for accepting lone-pair from π -bonding ligand.

Ex. $[\text{Ni}(\text{CO})_4]$, $[\text{Ag}(\text{CN})_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$

Colour Property

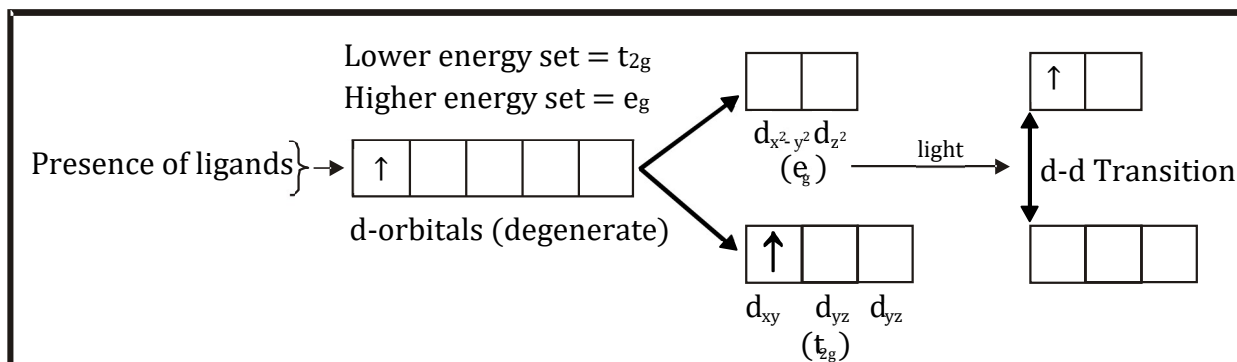
- (a) Most of the transition metal ions exhibit colour property.
- (b) This is due to d-d transition of unpaired electrons in their t_{2g} and e_g sets of 'd' orbitals.
- (c) They require less amount of energy to undergo excitation of electrons. Hence, they absorb visible region of light exhibiting colour.

Ex. $\text{Sc}^{+2} : [\text{Ar}]3d^1$, $\text{Ti}^{+2} : [\text{Ar}]3d^2$, $\text{V}^{+2} : [\text{Ar}]3d^3$

- (d) Transition metal ions which do not have any unpaired electrons in their 'd' orbitals like $3d^0$ and $3d^{10}$ configurations, do not exhibit any colour property.

Ex. $\text{Sc}^{+3} : [\text{Ar}]3d^0$, $\text{Cu}^{+1} : [\text{Ar}]3d^{10}$, $\text{Ti}^{+4} : [\text{Ar}]3d^0$ etc are colourless ions.

- (e) A transition metal ion selectively absorbs a portion of the visible light spectrum and releases the remaining colors, resulting in the emitted light's overall hue. The color of the metal ion corresponds to the emitted light's color.
- (f) In transition metal ion the 'd' orbitals split into lower energy set t_{2g} orbitals and higher energy set e_g orbitals. The electrons from t_{2g} set get excited to higher energy set e_g set. This excitation of electrons is called as 'd-d' transition. Due to this 'd -d' transition the transition metal ions exhibit colour property.



Factors affecting the colour of complex

The colour of a transition metal complex depends on-

- The magnitude of energy difference between the two d-levels (Δ_0),
- An increase in the magnitude of Δ_0 decreases the wave length (λ) of the light absorbed by the complexes.

$$\Delta_0 \propto \frac{1}{\lambda(\text{Wavelength of light absorb})}$$

- Thus, with a decrease in the λ the colour of complex changes from Red to Violet.

| | | | | | | | |
|------------|-------------------------------|--|---|-----------------------------------|---|---------------------------------|--|
| Ex. | Complex ions | $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ | | $[\text{Co}(\text{NH}_3)_6]^{3+}$ | | $[\text{Co}(\text{CN})_6]^{3-}$ | |
| | Ligand field strength | H_2O | < | NH_3 | < | CN^- | |
| | Magnitude of Δ_0 | $\Delta_0(\text{H}_2\text{O})$ | < | $\Delta_0(\text{NH}_3)$ | < | $\Delta_0(\text{CN}^-)$ | |
| | Magnitude of λ | $\lambda(\text{H}_2\text{O})$ | < | $\lambda(\text{NH}_3)$ | < | $\lambda(\text{CN}^-)$ | |
| | Colour of the transmitted | orange | | Green-blue | | violet | |
| | Colour of absorbed light | Green-blue | | Orange | | Yellow greenlight | |
| | (i.e., colour of the complex) | | | | | | |

- KMnO_4 (dark pink), $\text{K}_2\text{Cr}_2\text{O}_7$ (orange) having d^0 configuration but they are coloured due to charge transfer spectrum and charge is transferred from anion to cation.

Example of Some coloured metal ions:

| | | | |
|------------------|--------|------------------|------------|
| Ti^{+3} | Purple | Mn^{+2} | Light pink |
| Fe^{+3} | Yellow | Ni^{+2} | Green |

| | | | |
|------------------|------------|------------------|--------------|
| Sc ³⁺ | Colourless | Ti ³⁺ | Purple |
| V ³⁺ | Green | Cr ²⁺ | Blue |
| Mn ³⁺ | Violet | Fe ²⁺ | Green(light) |
| Co ²⁺ | Pink | Zn ²⁺ | Colourless |
| Cr ⁺³ | Green | Fe ⁺² | Green |
| Co ⁺³ | Pink | Cu ⁺² | Blue |
| Ti ⁴⁺ | Colourless | V ⁴⁺ | Blue |
| V ²⁺ | Violet | Cr ³⁺ | Green |
| Mn ²⁺ | Pink | Fe ³⁺ | Yellow |
| Ni ²⁺ | Blue | | |

Ex. Explain the blue colour of CuSO₄.5H₂O.

Sol. Cu²⁺ ion (3d⁹) absorbs red light from the visible region, for the promotion of 3d electrons, the ions reflect blue light and appear blue.

Magnetic Properties

- Typically, transition elements display magnetic properties. Para magnetism refers to the attraction of a substance to a magnetic field, primarily attributed to the existence of unpaired electrons in atoms, ions, or molecules. This property varies inversely with temperature.
- Diamagnetic substances are slightly repelled by a magnetic field, and this characteristic is temperature-independent.
- As is evident most of the transition metal ions have unpaired electrons in their 'd' orbitals. Hence most of the transition metal ions are paramagnetic in nature.

Ex. Ti⁺² [Ar]3d², Ti⁺³ [Ar]3d¹, V⁺²[Ar]3d³, Cr⁺³[Ar]3d³

- Transition metal ions having 3d⁰ and 3d¹⁰ configuration exhibit diamagnetic nature.
- The total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons.
- The magnetic moment (μ) created due to spinning of unpaired electrons can be calculated by using

$$\mu = \sqrt{n(n+2)}$$

Where - 'n' is the number of unpaired electrons in the metal ion.

μ = Magnetic moment in Bohr Magnetons (B.M.)

- (g) The magnetic moment of diamagnetic substances will be zero.
- (h) Transition metal ions with a d^5 configuration will exhibit maximum paramagnetic behavior due to the presence of the highest number of unpaired electrons.

Catalytic Property

- (a) Transition elements and their compounds exhibit catalytic properties. This is due to their variable valency as well as due to the free valencies on their surface.
- (b) When transition elements and their compounds are in powdered state, their catalytic properties exhibited will be to a greater extent. This is due to greater surface area available in the powdered state.
- (c) Transition metals and their compounds exhibiting catalytic properties in various processes are -

| Catalyst | Used |
|---|---|
| TiCl ₃ | Used as the Ziegler-Natta catalyst in the production of polythene. |
| MnO ₂ | Used as a catalyst to decompose KClO ₃ to give O ₂ |
| Fe | Promoted iron is used in the Haber-Bosch process for making NH ₃ |
| FeCl ₃ | Used in the production of CCl ₄ from CS and Cl ₂ |
| FeSO ₄ and H ₂ O ₂ | Used as Fenton's reagent for oxidizing alcohols to aldehydes. |
| PdCl ₂ | Wacker process for converting C ₂ H ₄ +H ₂ O+PdCl ₂ to CH ₃ CHO+2HCl+Pb. |
| pd | Used for hydrogenation (e.g., phenol to cyclohexanone). |
| Pt/ptO | Adams catalyst, used for reductions. |

| | |
|-------|---|
| Pt | Formerly used for $\text{SO}_2 \rightarrow \text{SO}_3$ in the contact process for making H_2SO_4 |
| Pt/Rh | Formerly used in the Ostwald process for making HNO_3 to NO |
| Cu | Is used in the direct process for manufacture of $(\text{CH}_3)_2\text{SiCl}_2$ used to make silicones. |
| Cu/V | Oxidation of cyclohexanol/cyclohexanone mixture to adipic acid which is used to make nylon-66 |
| CuCl | Decon process of making Cl from HCl |
| Ni | Raney nickel, numerous reduction processes (e.g., manufacture of hexamethylenediamine, production of H_2 from NH_3 reducing anthraquinone to anthraquinol in the production of H_2O_2) |