# D and f block elements

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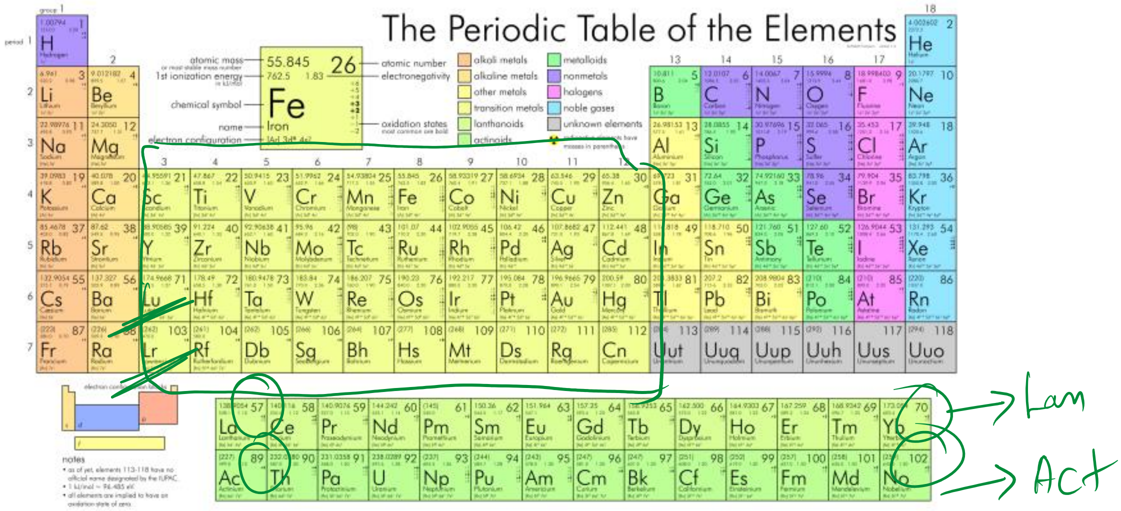


## General Characteristics of Transition Elements

### Electronic Configuration & Periodic Trends

- Transition elements **incompletely fill d-orbitals**, leading to unique properties.
- Across the period, **atomic and ionic radii decrease** due to increasing nuclear charge.
- **Density and hardness increase** with atomic number due to stronger metallic bonding. ✓

### Variable Oxidation States

- Due to the participation of both **(n-1)d and ns electrons** in bonding.
- Common oxidation states:
  - Sc → +3 ✓
  - Ti → +2, +3, +4
  - Mn → +2, +3, +4, +6, +7 ✓
  - Fe → +2, +3
  - Cu → +1, +2

### Metallic Bonding:

Transition elements exhibit metallic bonding due to their hexagonal close-packed (hcp), cubic close-packed (ccp), or body-centred cubic (bcc) crystal lattices. This bonding arises from the presence of one or two electrons in the outermost energy level (ns) and unpaired d-electrons.

### Ionisation Energies:

Ionisation energy generally increases with atomic number, though not in a regular pattern. For 5d-elements, ionisation energies are higher compared to 4d- and 3d-elements due to a greater effective nuclear charge caused by poor shielding by 4f-electrons.

### Electrode Potential ($E^\circ$):

The standard electrode potential, depends on three factors:

- **Heat of Sublimation** – The energy required to convert the solid metal into gaseous atoms.
- **Heat of Ionization** – The energy required to remove electrons from the gaseous metal atoms to form ions.
- **Heat of Hydration** – The energy released when gaseous metal ions dissolve in water to form hydrated ions.

$$E^0 (M^{2+}/M)$$

### High Melting and Boiling Points:

Transition metals have high melting and boiling points because of their strong metallic bonds. The melting point initially increases with atomic number, peaks, and then decreases as the atomic number rises further.

### Complex Formation:

Transition metals form numerous complexes due to the availability of vacant d-orbitals, small atomic size, and high charge density.

## Magnetic Properties:

These elements are paramagnetic owing to unpaired electrons. The magnetic moment (μ) is determined using the spin-only formula:

$$\mu_s = \sqrt{n(n+2)}\ BM$$

where n is the number of unpaired electrons.

## Alloy Formation:

Transition elements form alloys due to their similar atomic radii.

## Interstitial Compounds:

They form interstitial compounds by accommodating small atoms in the empty spaces within their crystal lattices.

### Table 1: Nature of Transition Metal Oxides

| **Metal** | **Oxide** | | |
|---|---|---|---|
| | **Basic** | **Amphoteric** | **Acidic** |
| Sc | $Sc_2O_3$ | - | - |
| Ti | $TiO$, $Ti_2O_3$ | $TiO_2$ | - |
| V | $VO$, $V_2O_3$ | $VO_2$ | $V_2O_5$ |
| Cr | $CrO$ | $Cr_2O_3$, $CrO_2$ | $CrO_3$ |
| Mn | $MnO$ | $Mn_3O_4$, $MnO_2$ | $Mn_2O_7$ |
| Fe | $FeO$, $Fe_2O_3$, $Fe_3O_4$ | - | - |
| Co | $CoO$ | - | - |
| Ni | $NiO$ | - | - |
| Cu | $Cu_2O$, $CuO$ | - | - |
| Zn | $ZnO$ | - | - |

22.
23
24
25

### Table 2: Relationship Between Oxidation Number and Acidity

| **Oxide** | **$MnO$** | **$Mn_3O_4$** | **$MnO_2$** | **$Mn_2O_7$** |
|---|---|---|---|---|
| Nature | Basic | Amphoteric | Amphoteric | Acidic |

**Note**: Acidic strength of oxides of a transition metal increases with increase in its oxidation number.

Color of d-Block Elements (Transition Metals)

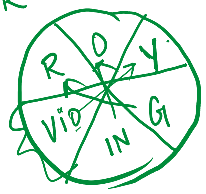
Reason for Color

The color of d-block elements is due to the d-d electronic transitions within the partially filled d-orbitals.

When light falls on a transition metal ion, some of the light energy

is absorbed to promote an electron from a lower d-orbital to a higher d-orbital (this is called d-d transition).
The remaining light is transmitted, and we see the complementary color of the absorbed wavelength.

VIBGYOR



Color of Some Common d-Block Ions

| Ion | Aqueous Solution Color |
|---|---|
| $Sc^{3+}$ | Colorless (No d-electrons) |
| $Ti^{3+}$ | Purple |
| $Ti^{4+}$ | Colorless (No d-electrons) |
| $V^{2+}$ | Violet |
| $V^{3+}$ | Green |
| $VO^{2+}$ | ($V^{4+}$) Blue |
| $VO_3^-$ | ($V^{5+}$) Yellow |
| $Cr^{2+}$ | Blue |
| $Cr^{3+}$ | Green |
| $Cr_2O_7^{2-}$ | (Dichromate) Orange |
| $CrO_4^{2-}$ | (Chromate) Yellow |
| $Mn^{2+}$ | Pale Pink |
| $MnO_4^{2-}$ | Green |
| $MnO_4^-$ | (Permanganate) Purple |
| $Fe^{2+}$ | Green |
| $Fe^{3+}$ | Yellow/Brown |
| $Co^{2+}$ | Pink |
| $Co^{3+}$ | Blue |
| $Ni^{2+}$ | Green |
| $Cu^{2+}$ | Blue |
| $Zn^{2+}$ | Colorless (Full $d^{10}$ configuration) |

Fully / partially
↓
Colourless.

Incomplete → Coloured

Colorless ions ($Sc^{3+}$, $Ti^{4+}$, $Zn^{2+}$) have no unpaired electrons and hence no d-d transitions occur.
The observed color is the complementary color of the absorbed light.

O.A → itself Reduction.

## $K_2\overset{+6}{Cr_2}O_7$ (Potassium Dichromate)

**Preparation**

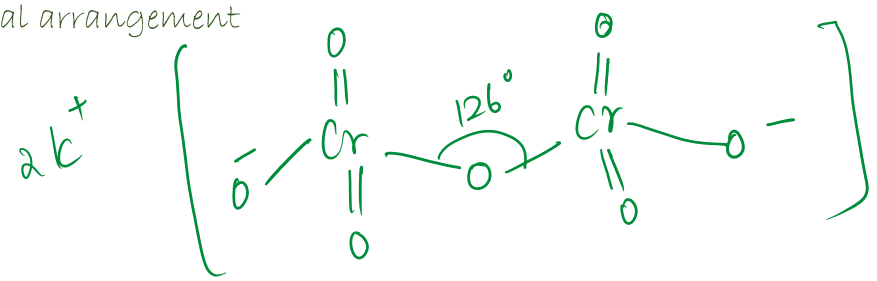
- $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
- $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

- $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

Orange .

## Structure

- Contains the dichromate ion ($Cr_2O_7^{2-}$)
- Two tetrahedral $CrO_4$ units sharing one oxygen atom
- Cr-O-Cr angle is approximately 126°
- Each chromium atom is surrounded by four oxygen atoms in tetrahedral arrangement



## Properties

1. **Physical Properties**:
   - ○ Orange-red crystalline compound
   - ○ Moderately soluble in cold water
   - ○ Freely soluble in hot water
2. **Chemical Properties**:
   - ○ **Thermal Decomposition**: $4K_2Cr_2O_7 \rightarrow 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$
   - ○ **Reaction with Alkali**:
     - ▪ Changes from orange-red to yellow due to chromate formation
     - ▪ $K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O$
   - ○ **Chromate-Dichromate Equilibrium**:
     - ▪ Interconvertible by changing pH
     - ▪ Acidification converts yellow chromate to orange dichromate: $2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$
     - ▪ Represented by the equilibrium: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} +$ $H_2O$ ✓ $H_2O$ (yellow) (orange)
   - ○ **Oxidizing Power**:
     - ▪ Powerful oxidizing agent, especially in acidic medium
     - ▪ One mole of $K_2Cr_2O_7$ in dilute $H_2SO_4$ provides three moles of nascent oxygen
     - ▪ $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

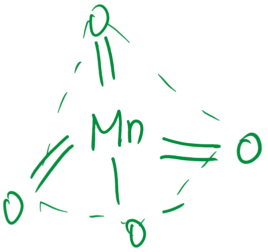
# $K\overset{+7}{Mn}O_4$ (Potassium Permanganate)

## Preparation

- $3K_2MnO_4 + 2H_2SO_4 \rightarrow 2K\overset{+6}{Mn}O_4 + \overset{+4}{Mn}O_2 + 2K_2SO_4 + 2H_2O$

## Structure

- Contains the permanganate ion ($MnO_4^-$)
- Tetrahedral geometry ✓
- Manganese is either $sp^3$ or $sd^3$ hybridized
- Can be considered as a mixture of $sp^3$ and $sd^3$ hybridization



## Properties

1. **Physical Properties**:
    - Dark purple crystalline compound
    - Moderately soluble in water, forming a purple solution
    - Solubility increases with temperature
2. **Chemical Properties**:
    - **Thermal Decomposition**:
        - Decomposes at 200°C: $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$
    - **Reaction with Alkalis**:
        - Decomposes upon heating with alkalies: $4KMnO_4 + 4KOH \rightarrow 4K_2MnO_4 + 2H_2O + O_2$ ✓
    - **Oxidizing Nature**:
        - Strong oxidizing agent in various media
        - **In Acidic Medium**: $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$ or: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
        - **In Alkaline Medium**: $2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O]$ or: $2MnO_4^- + H_2O + 3e^- \rightarrow 2\overset{+4}{Mn}O_2 + 2OH^- + 3[O]$
        - **In Neutral or Weak Acidic Solution**: $MnO_4^- + 2H_2O + 3e^- \rightarrow$

$MnO_2 + 4OH^-$

# f-BLOCK ELEMENTS (INNER-TRANSITION ELEMENTS)

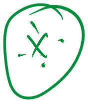
## General Characteristics

- Consists of two series:
  1. Lanthanides (lanthanoids)
  2. Actinides (actinoids)

## Lanthanides

## Electronic Configuration

- General outer electronic configuration: $4f^{1-1412}\ 5d^{0-1}\ 6s^2$



## Element Details

| Element | Atomic number | Electronic configuration | Oxidation states |
|---|---|---|---|
| La | 57 | $[Xe]5d^1 6s^2$ | +3 |
| Ce | 58 | $[Xe]4f^1 5d^1 6s^2$ | +3, +4 |
| Pr | 59 | $[Xe]4f^3 6s^2$ | +3, (+4) |
| Nd | 60 | $[Xe]4f^4 6s^2$ | (+2), +3, +4 |
| Pm | 61 | $[Xe]4f^5 6s^2$ | +3 |
| Sm | 62 | $[Xe]4f^6 6s^2$ | (+2), +3 |
| Eu | 63 | $[Xe]4f^7 6s^2$ | +2, +3 |
| Gd | 64 | $[Xe]4f^7 5d^1 6s^2$ | +3 |
| Tb | 65 | $[Xe]4f^9 6s^2$ | +3, +4 |
| Dy | 66 | $[Xe]4f^{10} 6s^2$ | +3, (+4) |
| Ho | 67 | $[Xe]4f^{11} 6s^2$ | +3 |

|  |  |  |  |
|---|---|---|---|
| Er | 68 | $[Xe]4f^{12}6s^2$ | +3 |
| Tm | 69 | $[Xe]4f^{13}6s^2$ | (+2), +3 |
| Yb | 70 | $[Xe]4f^{14}6s^2$ | +2, +3 |
| Lu | 71 | $[Xe]4f^{14}5d^16s^2$ | +3 |

## Lanthanide Contraction

- Definition: The decrease in size of atoms and ions with increase in atomic number in the lanthanide series
- Results from poor shielding effect of f-electrons

## Consequences of Lanthanide Contraction

1. **Chemical Effects**:
    - Decrease in basic strength of oxides and hydroxides from La to Lu ✓
    - Similar chemical properties across the series
    - Slight increase in electronegativity of trivalent ions from La to Lu ✓
    - Small increase in standard electrode potential values from La to Lu ✓
2. **Physical Effects**:
    - Decrease in atomic and ionic radii
    - Increase in density
    - Increase in melting and boiling points
    - Enhanced metallic character

## General Properties of Actinides

$5f^{1-14}\ 6d^{0-1}\ 7s^2$

### A. Oxidation States

- **Multiple oxidation states**: Several oxidation states are formed for each of the earlier members of this series
- **Transition element similarity**: Some actinides show great resemblance with elements of the transition series
- **Examples**:
    - Thorium shows a stable oxidation state of +4 and behaves like elements of Group 4

  - Uranium exhibits an oxidation state of +6 and resembles in many properties with elements of Group 6
- **Trend in +3 state**: The +3 oxidation state in actinoides becomes increasingly stable as atomic number increases

## B. Color and Paramagnetism

- **Color origin**: Cations of actinides with two or more 5f electrons are colored both in the crystalline state and in aqueous solutions
- **Examples**:
  - $U^{4+}$ is green ✓
  - $U^{3+}$ is red ✓
- **Magnetic behavior**:
  - Cations of actinides containing only paired electrons are diamagnetic
  - All other ions with unpaired 5f electrons are paramagnetic

## C. Ionic Sizes

- **Actinide contraction**: Similar to lanthanide contraction, due to poor shielding of the nuclear charge by 5f-electrons
- **Trend**: Ionic radii of trivalent cations decrease regularly with increase in atomic number across the series

Reason for Color

The color in f-block elements arises due to f-f electronic transitions within the partially filled f-orbitals.

Since f-electrons are deeply buried inside the atom (not exposed like d-electrons), the energy gaps between f-orbitals are smaller.

The color is weaker compared to transition metals.

Color of Some Lanthanide Ions

| Ion | Color |
|---|---|
| $La^{3+}$ | Colorless |
| $Ce^{3+}$ | Colorless |
| $Ce^{4+}$ | Yellow |
| $Pr^{3+}$ | Green |
| $Nd^{3+}$ | Purple |
| $Sm^{3+}$ | Yellow |
| $Eu^{3+}$ | Pink |
| $Gd^{3+}$ | Colorless |
| $Tb^{3+}$ | Green |

| | |
|---|---|
| $Dy^{3+}$ | Yellow |
| $Ho^{3+}$ | Pink |
| $Er^{3+}$ | Pink |
| $Tm^{3+}$ | Green |
| $Yb^{3+}$ | Colorless |

$La^{3+}$, $Ce^{3+}$, $Gd^{3+}$, $Lu^{3+}$ are colorless as they have empty or completely filled f-orbitals.
The colors are not as intense as transition metals because f-f transitions are forbidden by selection rules

## III. Differences between Lanthanoids and Actinoids

| | Lanthanoids | Actinoids |
|---|---|---|
| 1. | They show +2 and +4 oxidation states in few cases besides +3. | They show higher oxidation states of +4, +5, +6 and +7 besides +3. |
| 2. | Except promethium, they are non-radioactive. | All actinides are radioactive. |
| 3. | They do not form oxo-ions. | They form oxo-ions like $UO_2^{2+}$, $PuO_2^{2+}$, $UO_2^+$ etc. |
| 4. | The compounds of lanthanides are less basic. | Actinide compounds are more basic. |
| 5. | They have less tendency of complex formation. | They have greater tendency of complex formation. |

## Key Concepts of Transition and Lanthanide Elements

### Color of Transition Metal Ions

- Certain metal ions are colorless due to empty d-orbitals, preventing d-d transitions. Examples:
  $Sc^{3+}$, $Ti^{4+}$, $V^{5+}$, $Mn^{7+}$, $Cr^{6+}$ → Colorless (No d-d transitions)
  Some ions exhibit color due to charge transfer spectra:
  $VO_2^+$ → Pale Yellow
  $CrO_4^{2-}$ → Deep Yellow
  $MnO_4^-$ → Intense Purple
- **Wilkinson's Catalyst**

$MnO_4$ → Intense Purple

- **Wilkinson's Catalyst** ✗

  $[RhCl(PPh_3)_3]$ is known as Wilkinson's catalyst, featuring square planar geometry and widely used in the hydrogenation of alkenes.

- **Oxidation States of Transition Elements**

  The highest oxidation state found in a transition element is +8.
  Lower oxidation states (+2 and +3) tend to form ionic bonds, while higher oxidation states form covalent bonds.
  Transition metals can also exhibit low oxidation states like 0 and +1.

- **Biological Importance of Transition Elements** ✓

| Element | Biological Role |
|---|---|
| Fe | Hemoglobin (Oxygen transport in blood), Myoglobin (Oxygen storage in muscles) |
| Cu | Plastocyanin, Haemocyanin |
| Co | Vitamin $B_{12}$ |
| Zn | Carbonic Anhydrase |

- **Metallurgical and Industrial Applications**
- **Annealing**: Heating steel to red-hot and cooling slowly makes it soft.
- **Tempering:** Rapid cooling of heated steel (e.g., by plunging in ice-cold water) makes it hard and brittle.
- **Extraction of Silver from Coins/Ornaments**
- **Dissolution:**

  Coins (Ag-Cu alloy) are dissolved in $HNO_3$, forming metal nitrates.
  Separation:
  Boiling removes excess $HNO_3$, and treatment with HCl precipitates AgCl, leaving $Cu^{2+}$ in solution.

- **Reduction of AgCl to Silver:**

  $AgCl + H_2 \rightarrow Ag + HCl$
  $4AgCl + 2Na_2CO_3 \rightarrow 4Ag\downarrow + 4NaCl + 2CO_2 + O_2$
  $2AgCl + 2NaOH \rightarrow Ag_2O + 2NaCl + H_2O$
  $Ag_2O + C_6H_{12}O_6 \rightarrow 2Ag\downarrow + C_6H_{12}O_7$ (Glucose → Gluconic Acid)

- **Purification:**

  The extracted silver is purified by electrolysis.

  Oxidizing and Reducing Agents

  $Ce^{4+}$ solutions act as strong oxidizing agents.

  $Eu^{2+}$ and $Yb^{2+}$ are strong reducing agents in aqueous solutions.

- **Properties of Lanthanides**

  **Paramagnetism:** All lanthanide ions (except $La^{3+}$, $Lu^{3+}$, $Ce^{4+}$) are paramagnetic.

  **Complex Formation:**

  $(NH_3)_6CrO_4$ (formed in ammoniacal solution of $K_2Cr_2O_7$) is dark red-brown due to Cr(IV).

  **Industrial Uses:**

  Lanthanum oxides are used for polishing glass.

  Neodymium & Praseodymium oxides are used in making colored glass for goggles (absorbing yellow sodium light, useful for glassblowers.

- **Catalytic Applications:**
- Lanthanides serve as catalysts in hydrogenation, dehydrogenation, etc.
- **Medical Use:**
- Thorium salts are used in cancer treatment.
- Transition and Non-Transition Elements
- All transition elements belong to the d-block, but Zn, Cd, and Hg are not considered true transition elements due to their full $d^{10}$ configuration.

- **Color and Stability of Salts**
- $FeSO_4$ and $CuSO_4$ appear white in the anhydrous state because of the absence of crystal field splitting, despite having unpaired electrons.

- **Stability of Copper Ions:**

- $Cu^{2+}$ ($3d^9$) is more stable than $Cu^+$ ($3d^{10}$) in aqueous solutions:
- $E^\circ(Cu^{2+}/Cu) = 0.34$ V, while $E^\circ(Cu^+/Cu) = 0.54$ V.
- $Cu^+$ is more stable in presence of large anions.
- CuI is more stable than $CuI_2$, and CuCN is more stable than $Cu(CN)_2$.

- Interesting Facts
- Tungsten (W, Atomic No. 74) has the highest melting point (3410° C).
- Mercury (Hg, Atomic No. 80) has the lowest melting point (-38.9°C) among d-block elements.
- Technetium (Tc, Atomic No. 43) was the first artificially created element.

## JEE Main Questions

### Question 1 (JEE Main 2019)

The correct order of magnetic moments (spin only values in B.M.) among the following ions is:

(a) $Mn^{2+} > Cr^{3+} > Fe^{2+} > Ti^{3+}$

(b) $Ti^{3+} > Cr^{3+} > Fe^{2+} > Mn^{2+}$

(c) $Fe^{2+} > Mn^{2+} > Cr^{3+} > Ti^{3+}$

✓ (d) $Mn^{2+} > Fe^{2+} > Cr^{3+} > Ti^{3+}$

$Mn^{2+} - 3d^{\textcircled{5}}\ 4s^0$

$Cr^{3+} - 3d^{\textcircled{3}}\ 4s^0$

$Fe^{2+} - \overset{\textcircled{4}}{3d^6}\ 4s^0$

$Ti^{3+} - 3d^1\ 4s^0$

$$\mu = \sqrt{5(5+2)}$$
$$= \sqrt{5 \times 7} = \sqrt{35}$$
$$= \underline{5}.92$$

### Question 3 (JEE Main 2021)

The oxidation states of chromium in $\overset{+1}{K_3}[Cr(\overset{-2}{C_2O_4})_3]$ and $K_2[Cr\overset{-2}{O_4}]$ are respectively:

(a) +6 and +6

✓ (b) +3 and +6

(c) +6 and +3

$$3(+1) + x + 3(-2) = 0$$
$$+ x - 6 = 0$$

[✓ (b)] +3 and +6
(c) +6 and +3
(d) +3 and +3

$3(+1)+x$

$3+x-6=0$

$x=+6-3$

$x=+3$

$2(+1)+x+4(-2)=0$

$2+x+(-8)=0$

$x=+8-2$

$x=+6$

## JEE Advanced Questions

### Question 4 (JEE Advanced 2018)

Among the following, the number of compounds that liberate $CO_2$ on treatment with dilute acid is: $K_2CO_3$ ①, $Na_2O_2$ ✗, $Fe_2(CO_3)_3$ ②, $BaO_2$ ⊗, CaO ⊗, $Mn_2O_3$ ⊗

[✓ (a)] 2 (b) 3 (c) 4 (d) 5

### Question 6 (JEE Advanced 2017)

Identify the correct statements from the following:

[✓ (a)] The lanthanide contraction is responsible for the fact that the atomic radii of Zr and Hf are almost identical
[✓ (b)] The actinides exhibit more oxidation states than the lanthanides
[✓ (c)] In the lanthanide series, the ionic radius of $Eu^{2+}$ is larger than that of $La^{3+}$
[✓ (d)] Lanthanides form colored ions because of partly filled f orbitals

(c) In the lanthanide series, the ionic radius of $Eu^{2+}$ is larger than that of $La^{3+}$

(d) Lanthanides form colored ions because of partly filled f-orbitals

## Question 7 (JEE Advanced 2020)

Which of the following statements is/are correct?

(a) $Ce^{4+}$ ion is a good oxidizing agent ✓

(b) $Eu^{2+}$ ion is a good reducing agent ✓ ⑦ ⑥

(c) The magnetic moment of $Gd^{3+}$ is higher than that of $Eu^{3+}$

(d) The basicity of $Ln(OH)_3$ decreases from La to Lu

**Question 8 (JEE Advanced 2021)**

When $MnO_4^-$ reacts with $SO_2$ in acidic medium, the oxidation state of Mn changes from:

[✓ (a) +7 to +2] (b) +7 to +4 ~~(c)~~ +4 to +7 ~~(d) +4~~ to +2

$$2\overset{+7}{Mn}O_4^- + 5SO_2 + H_2O \longrightarrow Mn^{2+} + 5SO_4^{2-} + 4H^+$$