



CHEMISTRY • CLASS 12

CHAPTER 4

The d- and f-Block Elements

NCERT SOLUTIONS

ELECTRON CONFIGURATIONS OF EIGHT IONS

4.1 Write electronic configurations of (i) Cr^{3+} , (ii) Pm^{3+} , (iii) Cu^+ , (iv) Ce^{4+} , (v) Co^{2+} , (vi) Lu^{2+} , (vii) Mn^{2+} , (viii) Th^{4+} .

Solution:

Ion	Electronic configuration	Ion	Electronic configuration
(i) Cr^{3+}	$[\text{Ar}] 3d^3$	(ii) Pm^{3+}	$[\text{Xe}] 4f^4$
(iii) Cu^+	$[\text{Ar}] 3d^{10}$	(iv) Ce^{4+}	$[\text{Xe}] (4f^0)$
(v) Co^{2+}	$[\text{Ar}] 3d^7$	(vi) Lu^{2+}	$[\text{Xe}] 4f^{14} 5d^1$
(vii) Mn^{2+}	$[\text{Ar}] 3d^5$	(viii) Th^{4+}	$[\text{Rn}] (5f^0)$

In forming cations, outer ns electrons are removed before $(n-1)d$ or $4f$ electrons.

WHY SOME +2 IONS ARE MORE STABLE

4.2 Why is Mn^{2+} more resistant than Fe^{2+} to oxidation to +3?

Solution: Mn^{2+} has the electronic configuration $[\text{Ar}] 3d^5$, which is a half-filled d-subshell and therefore extra stable. Oxidation to +3 would give Mn^{3+} with configuration $[\text{Ar}] 3d^4$, which loses this half-filled stability, so Mn^{2+} is more resistant to oxidation.

Fe^{2+} has the configuration $[\text{Ar}] 3d^6$. Oxidation to +3 gives Fe^{3+} with configuration $[\text{Ar}] 3d^5$, which is a half-filled and more stable arrangement. Hence Fe^{2+} oxidises more readily to Fe^{3+} than Mn^{2+} .

4.3 Why does +2 state become more stable from Sc toward Mn in first half of first transition row?

Solution: For M^{2+} , the configurations progress as follows from Sc to Mn:



Across the series, the effective nuclear charge increases, so the d electrons are held more strongly and removal of another d electron (to form M^{3+}) becomes progressively harder. In addition, Mn^{2+} has the especially stable half-filled $3d^5$ configuration, making it the most stable +2 ion in this half of the series.

This is a broad trend, and does not mean that all +2 ions have equal stability in solution.

CONFIGURATION AND OXIDATION-STATE STABILITY

4.4 How far do electronic configurations decide the oxidation-state stability in the first transition series? Give examples.

Solution: Electronic configurations such as d^0 , d^3 , d^5 and d^{10} can help stabilise certain oxidation states in the first transition series, but they are not the only factor. The actual stability of an oxidation state also depends on ionisation energies, hydration energies, lattice energies and ligand (crystal field) stabilisation energies, along with the particular chemical environment.

Examples:

- Mn^{2+} : $[\text{Ar}] 3d^5 \rightarrow d^5$ configuration; relatively stable ion.
- Fe^{3+} : $[\text{Ar}] 3d^5 \rightarrow d^5$ configuration; relatively stable ion.
- Cr^{3+} : $[\text{Ar}] 3d^3 \rightarrow d^3$ configuration; particularly stable in aqueous solution (high hydration energy).
- Cu^+ : $[\text{Ar}] 3d^{10} \rightarrow d^{10}$ configuration, but not stable in aqueous solution; it disproportionates:
$$2\text{Cu}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{Cu}(\text{s})$$

Cause → Effect

Electronic configuration
(d^0 , d^3 , d^5 , d^{10})



Can give extra stability
(to certain ions)



But stability also depends
on ionisation, hydration,
lattice and ligand energies.

CAN A GROUND-STATE d COUNT PREDICT AN ION?

4.5 What are the likely stable oxidation states for neutral first-row transition elements with ground-state d counts $3d^3$, $3d^5$, $3d^8$ and $3d^4$?

Solution: The likely stable oxidation states are as follows:

Ground-state d count	Element (ground-state configuration)	Likely stable oxidation state(s)	Reasoning
$3d^3$	V ($3d^3 4s^2$)	+3, +4, +5	All three oxidation states occur for V. +5 is common in oxoanions (e.g., VO_4^{3-}).
$3d^5$	Mn ($3d^5 4s^2$) (Cr: $3d^5 4s^1$)	+2 (favoured), +7	Mn^{2+} (d^5) is especially stable (half-filled d). +7 occurs in MnO_4^- . Cr ($3d^5 4s^1$) commonly shows +3 and +6.
$3d^8$	Ni ($3d^8 4s^2$)	+2	Ni^{2+} (d^8) is the most common and stable oxidation state for Ni.
$3d^4$	— (No first-row neutral atom has $3d^4$ ground state)	No unique oxidation state can be assigned.	There is no first-series neutral atom with a $3d^4$ ground state. Chromium is an exception with configuration $3d^5 4s^1$, not $3d^4 4s^2$.

Thus, a ground-state d count gives a useful indication of possible oxidation states, but it does not fix a unique oxidation state for an ion.

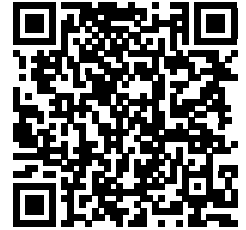


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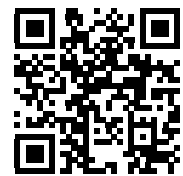


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