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TOPIC: - RELATIVE STABILITY OF OXIDATION STATES OF THE ELEMENTS OF FIRST TRANSITION SERIES

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The stability of an element is determined by its electronic configuration. The elements of the 3d-transition series, generally exhibit variable oxidation states and are more stable in a particular oxidation state, e.g., $Ti^{4+} > Ti^{3+}$ and $Fe^{3+} > Fe^{2+}$ etc. Generally, lower oxidation states are less stable than the higher oxidation states. This relative stability depends on many factors:

(a) Filled, half-filled and vacant d-orbitals present in the compound, i.e. d^{10}, d^5 and d^0 configurations are more stable than other configurations, e.g. $Ti^{4+}(d^0) > Ti^{3+}(d^1)$; $Mn^{2+}(d^5) > Mn^{3+}(d^4)$. However, it is not always true, e.g. $Cu^{+}(3d^{10})$ is less stable than $Cu^{2+}(3d^9)$ due to high lattice energy and solvation energies of Cu^{2+} in solid state and in solution.

(b) Higher oxidation states become less stable as atomic number increases. For example, $Sc^{3+} > Ti^{3+} > V^{3+} >$ ----------------> $Ni^{3+} > Cu^{3+}$.

In the binary compounds of elements of 3d-transition series, it has been observed that halogens and oxygen also illustrate the trend in stability. Generally, the group oxidation state for many elements is brought out more readily by oxygen than fluorine, the strongest halogen. This may be because fewer oxygen atoms are required than fluorine atoms to achieve the same oxidation state. For example, the group oxidation state (+7) of Mn is achieved in MnO_4^-, but MnF_7 has never been prepared. In the d-block elements, the oxidation states can be stabilised by complex formation. Low oxidation states are less stable and ligands like CN^-, N_2, NO, CO, C_6H_6, C_2H_4 etc. called π-acceptors form complexes in these low oxidation states to stabilise them. These complexes are known as π-complexes,

e.g. $[Ni(CO)_4]$, $[Cr(C_6H_6)_2]$, $[Fe(C_5H_5)_2]$ etc.

Higher oxidation states are stabilized by complex formation with highly electronegative ligands.
The compounds in any oxidation state of the metal are regarded as stable if they have free existence, are not oxidised by air, are not hydrolysed by water vapour, do not disproportionate or decompose at normal temperature.