

Differences between 1st, 2nd and 3rd row TMs

- (1) Early TM complexes more air sensitive and less functional group tolerant.
- (2) Group 3 and the lanthanides show very little redox chemistry and only 1-electron processes (only Sm^{III/II}, Eu^{III/II}, Yb^{III/II}, Ce^{III/IV}).
- (3) Highest oxidation states and the greatest range of oxidation states found for the mid transition metals (groups 5-9).

Most common oxidation states for 1st row TMs

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	0	0	0	0	0	0	0	[0]	
		1	1	1	1	1	1	1	
	2	2	2	2	2	2	2	2	2
3	3	3	3	3	3	3	3	3	
	4	4	4	4	4	4	4	[4]	
		5	5	5					
			6	6	6				
				7					

Differences between 1st, 2nd and 3rd row TMs

- (1) Ionic Radii – 1st row small (Ti⁴⁺ 0.745 Å), 2nd and 3rd row larger but similar to one another (Zr⁴⁺ = 0.860 Å, Hf⁴⁺ = 0.850 Å).
- (2) Higher oxidation states more accessible down a group (d-orbitals further from the nucleus) (MnO₄⁻ = good oxidant, ReO₄⁻ = poor oxidant).
- (3) 1st row TMs have smaller ligand field splitting energies → High Spin complexes possible, less likely to obey 18-electron rule.
- (4) 1st row TMs exhibit more 1-electron redox processes (e.g. Fe^{II/III} or Co^{I/II}) while 2-electron processes (Rh^{I/III}, Pt^{0/II/IV}) dominate in 2nd row TM chemistry.
- (5) 1st row TMs are less prone to M-M bonding.
- (6) 1st row TM chemistry involves more paramagnetic complexes → paramagnetic chemistry quite challenging (no NMR), so less well understood.
- (7) Spin-orbit coupling much less significant for 1st row TM complexes → allows simple interpretation of UV-Vis spectra and magnetic moment measurements.
- (8) Ligands less labile for 3rd row TM complexes compared with 2nd row TM complexes – 2nd row TM complexes often best for catalysis.