

CHEMISTRY OF ELEMENTS OF 1ST TRANSITION SERIES

Prepared by:

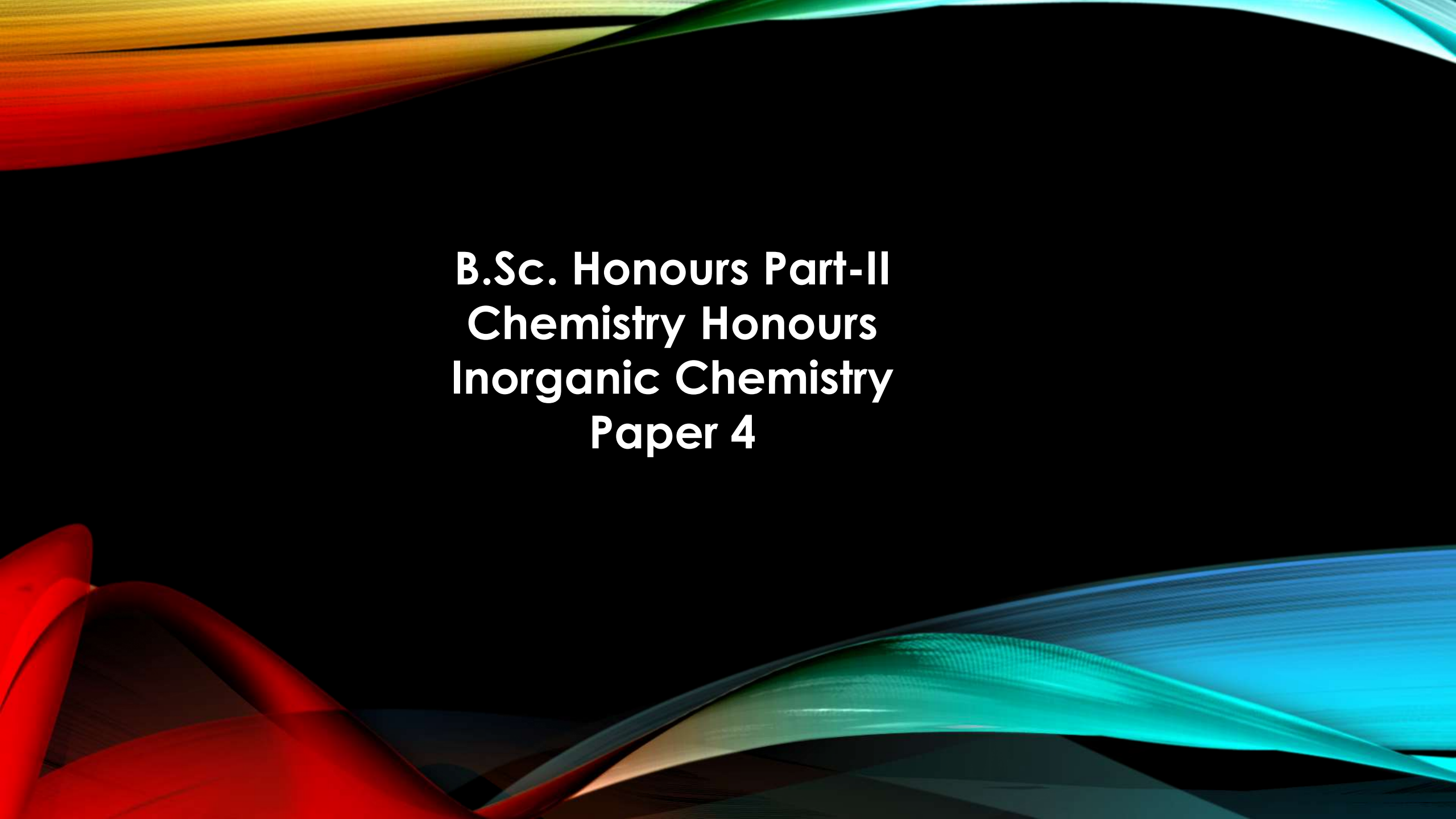
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**B.Sc. Honours Part-II
Chemistry Honours
Inorganic Chemistry
Paper 4**

CHEMICAL PROPERTIES OF FIRST ROW IN TRANSITION ELEMENTS

LEARNING OUTCOME

EXPLAIN IN VARIABLE OXIDATION STATES IN TERMS OF THE ENERGIES OF 3d AND 4s ORBITALS.

1-2	3	4	5	6	7	8	9	10	11	12	13-18
s-block	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	p-block
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	

OCCURANCE OF VARIABLE OXIDATION STATES

- Most obvious characteristics chemical properties of the transition metals is the occurrence of variable oxidation states.
- All transition metals from titanium to copper exhibit two or more oxidation states in their compounds. The small energy difference between the 3d and 4s subshells enable the electrons from the 4s as well as a variable number of electrons from the 3d subshell to be involved in bonding.

The wide range of oxidation states shown by the transition elements . More to known as oxidation states of the first d-block series .

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					

- From scandium to manganese , the maximum oxidation states increases , corresponding to the involvement of all the electrons in the 3d and 4s orbitals. That is , form +3 in scandium to +7 in manganese.
- Conversely , the maximum oxidation states decreases from manganese to zinc . This is because the pairing of *d* electrons occurs after manganese based on Hund's rule which in turn decreases the number of available unpaired electrons. Hence, the number of oxidation states decreases from +7 in manganese to +2 in zinc.

Hund's Rule

States that the most stable arrangement of electrons in degenerate orbitals is the one with the greatest number of parallel spins.

When filling a set of degenerate orbitals , no pairing of electron can take place until each orbital in the set has an electron.


OXO IONS OF TRANSITION ELEMENTS

- 1) Transition elements in lower oxidation states (+1,+2,+3) exist as simple ions.
- 2) However , transition elements do not form simple ions in higher oxidation states (+4 to +7) .

WHY?

→ This is due to too much of energy would required to remove so many electrons and would result in ions of extremely high charge density.

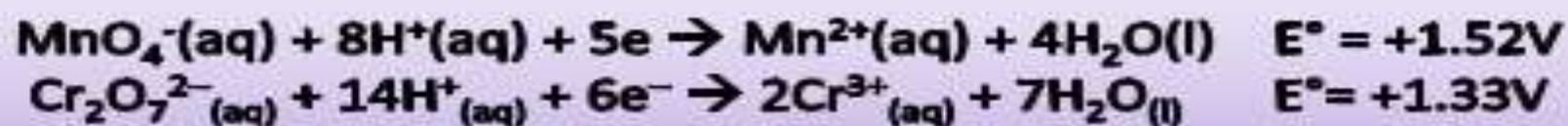
- 3) Compounds or ions containing transition elements in **higher oxidation states are usually bonded covalently to electronegative elements** like oxygen or fluorine to form Oxo ions .



Oxoanion where any ion that combined with Oxygen or Fluorine.

4) Transition metal ions in higher oxidation states have covalent characteristics and tend to make good oxidising agents.

→ The purple Manganate (VII) ion and the orange Dichromate (VI) ion are familiar oxidising agents. Their oxidising power is indicated by the highly positive standard electrode potentials.



5) There is a tendency for intermediate oxidation states to disproportionate.

6) Stability of a particular oxidation state may be affected by the pH of a solution.



MnO₄²⁻ is stable in alkaline solution but decomposes rapidly to MnO₄⁻ in acidic solutions.

Disproportionation is a specific type of redox reaction in which a species is simultaneously reduced and oxidised to form two different products.

OXIDES OF TRANSITION ELEMENTS

- Most transition metals react with oxygen to form oxides. The oxides are nearly all insoluble in water with **appreciable covalent character**. The oxides are either black or coloured .



- Transition elements with low oxidation states (+2 and +3) usually form **basic electrovalent oxides**, whereas those with higher oxidation states usually form **acidic covalent oxides** .




+2 and +3 OXIDATION STATES

- The most common oxidation states are +2 and +3. All the transition elements from titanium to copper exhibit both these two oxidation states in their compounds.
- The relative stability of +2 oxidation state increases but the stability of +3 state decreases across the period.

WHY?

→ The increase of nuclear charge binds the *d*-subshell electrons more strongly, thereby increasing the difficulty of removing the third electron from the *d* orbital.

- The relative stabilities of the +2 and +3 oxidation states in aqueous solutions can be predicted based on the standard electrode potentials.
- A graphical method may be used to compare the relative stabilities of +2 and +3 oxidation solutions. The E° values for the M^{2+}/M and M^{3+}/M^{2+} systems are represented in graph 

- The **negative standard electrode potentials M^{3+}/M^{2+}** for titanium, vanadium and chromium indicate that the higher oxidation state +3 is more stable for Ti, V and Cr.
- The **positive standard electrode potential of Mn^{3+}/Mn^{2+} and Co^{3+}/Co^{2+}** indicates that Mn^{2+} and Co^{2+} are the stable states in aqueous solution.
- In the absence of oxygen, Fe^{2+} ion is the stable state in aqueous solution. However, in the presence of oxygen in air, the Fe^{2+} ion is unstable and will be further oxidised to Fe^{3+} ion.
- The **+2 ions start as strong reducing agents and become more stable across the period.** Whereas the **+3 ions start stable and become more oxidising across the period.**

Mn^{3+} and Co^{3+} ions, being strong oxidising agents, can react with water spontaneously releasing oxygen.