# **Quadrant II – Transcript and Related Materials**

**Programme : Bachelor of Science (Second Year)** 

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Module Name : General characteristic properties of 3d series with special reference to electronic configuration, variable valency

Name of the Presenter : Chandan C. Naik, Ph.D.

#### Notes

### **3d Series**

- 1. The 3d series begins with scandium (At. No. 21) and ends at Zinc (At. No. 30).
- 2. These elements have incompletely filled d-subshell in their ground state or most stable oxidation state and are named as d-block or transition elements.
- 3. Zinc does not have partially filled d subshell either in the elemental state or in any of their common ions. Therefore, it is not a transition element.



## **3d Series: General Properties**

- 1. Their general characteristic properties of 3d series are intermediate between those of the s-block and p-block elements.
- 2. The elements of the 3d-series are metallic in nature.
- 3. They are hard, ductile and malleable.
- 4. They are good conductors of heat and electricity.
- 5. They are hard and due to the presence of strong interatomic bonds and compact crystal structure, they possess a high melting point and boiling point.
- 6. Densities of elements in 3d series are quite high (Greater than 5 g cm<sup>-3</sup>).
- 7. The atomic radii and ionic radii decrease gradually with increase in atomic number.
- 8. The ionization energies of elements in the 3d series are fairly high.
- 9. Elements in 3d series have the tendency to form complexes.
- 10. The compounds and complexes of elements in 3d series are coloured in the solid and solution state.
- 11. They are good reducing agents, however, they are not as good reducing agents as the metals of groups 1, 2 & 13.
- 12. They form alloys with other compounds.
- 13. The 3d series elements and their compounds have good catalytic activity.
  - e.g. i. Haber's Process: Fe catalyst
    - ii. Contact process: V<sub>2</sub>O<sub>5</sub> catalyst

#### **3d Series: Electronic Configuration**

1. The general electronic configuration of the 3d series is

### [Ar] 3d<sup>1-10</sup> 4s<sup>1-2</sup>

- 2. The d-orbitals may have one to ten electrons and the s-orbital of the outermost shell may have one or two electrons.
- 3. After filling of 4s orbital successively with two electrons at atomic number 19 and 20, the next incoming electron goes to 3d orbital instead of 4p, as the 3d orbital is of lower energy than the 4p orbital.
- 4. Sc is the first member of the 3d series and its electronic configuration is [Ar]  $3d^1 4s^2$ .
- In subsequent elements, the 3d orbitals get completely filled up with electrons up to Zinc [Ar] 3d<sup>10</sup> 4s<sup>2</sup>.
- 6. In Cr the expected configuration is [Ar] 3d<sup>4</sup>4s<sup>2</sup>. However, the spectral analysis of Cr

suggests that the configuration is [Ar] 3d<sup>5</sup>4s<sup>1</sup>.

In Cu the expected configuration is [Ar] 3d<sup>9</sup>4s<sup>2</sup>. However, the spectral analysis of Cu suggests that the configuration is [Ar] 3d<sup>10</sup>4s<sup>1</sup>.

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>1</sup> 4s <sup>2</sup>
Titanium	Ti	22	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>2</sup> 4s <sup>2</sup>
Vanadium	V	23	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>3</sup> 4s <sup>2</sup>
Chromium	Cr	24	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup> 4s <sup>1</sup>
Manganese	Mn	25	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>5</sup> 4s <sup>2</sup>
Iron	Fe	26	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>6</sup> 4s <sup>2</sup>
Cobalt	Со	27	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>7</sup> 4s <sup>2</sup>
Nickel	Ni	28	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>8</sup> 4s <sup>2</sup>
Copper	Cu	29	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>1</sup>
Zinc	Zn	30	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup>

## The occurrence of Variable Oxidation States

- Elements in 3d series (except Zinc) exhibit two or more oxidation states in their compounds.
- The variable oxidation states is mainly due to the availability of 3d orbital electrons in addition to 4s orbital electrons for bonding.
- The stability of a particular oxidation state is related to the electronic configuration.
- Thus Sc<sup>3+</sup> and Ti<sup>4+</sup> are stable because of the highly stable unfilled 3d<sup>0</sup> configuration.
- The stability of Mn<sup>2+</sup> and Fe<sup>3+</sup> is due to the special stability of half-filled 3d<sup>5</sup> configuration.
- Zinc shows only Zn<sup>2+</sup> state because of highly stable 3d<sup>10</sup> configuration.

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

## **Oxidation States of Elements in 3d Series**

## +2 And +3 Oxidation States

- 1. The most common oxidation states are +2 and +3.
- 2. The stability of +2 oxidation state increases with increase in atomic number.
- 3. The 3d series show +2 oxidation state when both the 4s electrons are involved in bonding
- 4. The oxidation state greater than +2 is exhibited by utilizing the 4s and 3d electrons.
- 5. Ti, V and Cr are the strong oxidising agent in this state.
- 6. In the case of Mn 2+ state is easily obtained and it is difficult to oxidise it to higher oxidation state because of special stability of half-filled d5 configuration of Mn2+ ion.
- 7. Transition elements with low oxidation states (+2 and +3) usually form basic electrovalent oxides.
- 8. In the absence of oxygen, Fe<sup>2+</sup> ion is the stable state in aqueous solution. However, in the presence of oxygen in the air, the Fe<sup>2+</sup> ion is unstable and will be further oxidised to Fe<sup>3+</sup> ion.
- 9. Sc readily exhibits this oxidation state, however, this oxidation state is not stable for manganese, cobalt and Nickel
- 10. Cr exhibit stable 3+ oxidation state.

### The oxidation state of 4+

- 1. This oxidation state is not common in the 3d series.
- 2. Ti and V show this oxidation state.
- 3. Manganese exhibit this oxidation state on MnO2 which is amphoteric in nature.

4. Ti and V oxides are acidic in nature.

## The oxidation state of 6+ and 7+

- 1. The higher oxidation state from 3+ to 7+ is because of the utilization of all 4s and 3d electrons in the transition series of elements.
- 2. Higher oxidation state has oxidising properties.
- Thus K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Cr<sup>6+</sup>) and KMnO<sub>4</sub> (Mn<sup>7+</sup>) are good oxidising agents and are readily reduced to Cr<sup>3+</sup> and Mn<sup>2+</sup> respectively.
- 4. Cr exhibit 6+ oxidation state of in K<sub>2</sub>CrO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. These compounds are good oxidising agents.
- 5. Similarly manganese exhibit 6+ oxidation state in K<sub>2</sub>MnO<sub>4</sub> and 7+ in KMnO<sub>4</sub>.
- 6. KMnO<sub>4</sub> is a stable compound and a powerful oxidising agent.
- 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.
- 8. Transition metal ions in higher oxidation states have covalent characteristics and tend to make good oxidising agents.
- 9. For example, the purple Manganate (VII) ion and the orange dichromate (VI) ion are familiar oxidising agents.
- 10. In general, lower oxidation states of these metals give basic oxides and the higher oxidation states give acidic oxides.
- 11. The intermediate oxidation states are generally amphoteric.

Manganese Oxide	<b>Oxidation State</b>	Nature of Oxide
MnO	+2	Basic
Mn <sub>2</sub> O <sub>3</sub>	+3	Basic
MnO <sub>2</sub>	+4	Amphoteric
Mn <sub>2</sub> O <sub>7</sub>	+7	Acidic

## Dependence of colour on the oxidation state

- The colour of the same metal changes with change in oxidation state. This is mainly because of the different no. of electrons are associated and the energy for excitation of electrons also differs
- Cuprous Cu<sup>1+</sup> colourless: completed 3d shell

- Cupric Cu<sup>2+</sup> coloured: Incomplete 3d shell, hence transition can take place in the same subshell thus involving small energy and hence causing absorption in the visible spectrum.
- For example, the different oxidation state of vanadium gives different colours.

<b>V</b> <sup>5+</sup>	V <sup>4+</sup>	<b>V</b> <sup>3+</sup>	V <sup>2+</sup>
Yellow	Blue	Green	Violet