Written as per the revised syllabus prescribed by the Maharashtra State Board of Secondary and Higher Secondary Education, Pune.

Precise

Chemistry – II

STD. XII Sci.

Salient Features

- Concise coverage of syllabus in Question Answer Format.
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'Chapters 1 to 7 are a part of Std. XII: Precise Chemistry - I'

Note: All the Textual questions are represented by * mark.
All the Intext questions are represented by # mark.

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d-Block Elements

8.1 General introduction and electronic configuration

***Q.1. What are d-block elements?**

Ans: *The elements in which the last electron enters the d-orbital of the penultimate shell i.e.,(n−1)d-orbital where 'n' is the outermost shell, are called* ***d-block elements.***

Their general valence or outer electronic configuration is $(n-1)d^{1-10}ns^{1-2}$.

***Q.2. Explain the position of d-block elements in the periodic table.**

Ans: Position of d-block elements in the periodic table:

i. The d-block elements lie in between s- and p-block elements, i.e., these elements are located in the middle part of the periodic table.

ii. The d-block elements are present in 4th period (Sc to Zn, 10 elements), 5th period (Y to Cd, 10 elements), 6th period (La, Hf to Hg, 10 elements) and 7th period (Ac, Rf to Uub, 10 elements)

iii. d-block elements are present from group 3 to group 12.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		d-block										p-block					
4	19	20	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31	32	33	34	35	36
5	37	38	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49	50	51	52	53	54
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Position of d-block elements in the periodic table

Q.3. Why are d-block elements called transition elements? **(NCERT)**

Ans: i. ***Transition elements*** *are defined as those elements which have partly or incompletely filled (n−1)d orbitals in their elementary state or in any of their common oxidation states.*

ii. The 3d, 4d, 5d and 6d series of the d-block elements correspond to the filling of 3d, 4d, 5d and 6d orbitals of the $(n - 1)^{th}$ main shell. The last electron enters the (n – 1) d-orbital.

iii. d-block elements are called transition elements as they show transition in the properties from the most electropositive s-block elements to the less electropositive p-block elements.

Q.4. *Explain the meaning of transition series. OR Explain in brief, four series of transition elements.

Ans: i. d-block elements are also known as transition elements. The long form of periodic table contains four series of transition elements, known as transition series.

ii. Four transition series are 3d, 4d, 5d and 6d series wherein orbitals of $(n - 1)^{th}$ main shell gets filled.

a. The 3d series contains the elements from Sc (Z = 21) to Zn (Z = 30) belonging to the 4^{th} period.
b. The 4d series contains the elements from Y (Z = 39) to Cd (Z = 48) belonging to the 5^{th} period.
c. The 5d series begins with La (Z = 57) and contains elements from Hf (Z = 72) to Hg (Z = 80) belonging to the 6^{th} period.
d. The 6d series begins with Ac (Z = 89) and contains elements from Rf (Z = 104) to Uub (Z = 112) belonging to the 7^{th} period.

Q.5. Give the general electronic configuration of four series of d-block elements.

Ans: d-block elements have general valence electronic configuration $(n - 1)d^{1-10}\ ns^{1-2}$.

The four series of d-block elements have the general electronic configuration as shown below:

i. 3d series: $[Ar]\ 3d^{1-10}\ 4s^{1-2}$
ii. 4d series: $[Kr]\ 4d^{1-10}\ 5s^{0-2}$
iii. 5d series: $[Xe]\ 5d^{1-10}\ 6s^{2}$
iv. 6d series: $[Rn]\ 6d^{1-10}\ 7s^{2}$

Note: Electronic configuration of the elements belonging to the 3d series of d-block elements:

3d series or First Row Transition Series (Sc to Zn)				
Elements	**Symbols**	**Atomic number**	**Expected electronic configuration**	**Observed electronic configuration**
Scandium	Sc	21	$[Ar]\ 3d^1\ 4s^2$	$[Ar]\ 3d^1\ 4s^2$
Titanium	Ti	22	$[Ar]\ 3d^2\ 4s^2$	$[Ar]\ 3d^2\ 4s^2$
Vanadium	V	23	$[Ar]\ 3d^3\ 4s^2$	$[Ar]\ 3d^3\ 4s^2$
Chromium	Cr	24	$[Ar]\ 3d^4\ 4s^2$	$[Ar]\ 3d^5\ 4s^1$
Manganese	Mn	25	$[Ar]\ 3d^5\ 4s^2$	$[Ar]\ 3d^5\ 4s^2$
Iron	Fe	26	$[Ar]\ 3d^6\ 4s^2$	$[Ar]\ 3d^6\ 4s^2$
Cobalt	Co	27	$[Ar]\ 3d^7\ 4s^2$	$[Ar]\ 3d^7\ 4s^2$
Nickel	Ni	28	$[Ar]\ 3d^8\ 4s^2$	$[Ar]\ 3d^8\ 4s^2$
Copper	Cu	29	$[Ar]\ 3d^9\ 4s^2$	$[Ar]\ 3d^{10}\ 4s^1$
Zinc	Zn	30	$[Ar]\ 3d^{10}\ 4s^2$	$[Ar]\ 3d^{10}\ 4s^2$

$[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

#Q.6. In which period of the periodic table, will an element, be found whose differentiating electron is a 4d electron?

Ans: Fifth period of the periodic table consist of elements in which the differentiating electron is a 4d electron.

Q.7. Write observed electronic configuration of elements from first transition series having half filled d-orbitals. **[Oct 13]**

Ans:

Element	**Symbol**	**Atomic Number**	**Expected Electronic Configuration**	**Observed Electronic Configuration**
Chromium	Cr	24	$[Ar]\ 3d^4\ 4s^2$	$[Ar]\ 3d^5\ 4s^1$
Manganese	Mn	25	$[Ar]\ 3d^5\ 4s^2$	$[Ar]\ 3d^5\ 4s^2$

$[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ *[Electronic configuration of elements – **1 Mark each**]*

***Q.8. Why does copper show abnormal electronic configuration?**

Ans: Copper has atomic number 29. Its expected and actual electronic configurations are:

$_{29}$Cu (Expected): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^9\ 4s^2}$

(Actual): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^{10}\ 4s^1}$

Explanation:

i. The energy difference between the 3d and 4s orbitals is very low.

ii. The d-orbital being degenerate, acquires more stability when it is half-filled ($3d^5$) or completely filled ($3d^{10}$).

iii. Due to the inter-electronic repulsion, one electron from the 4s orbital is transferred to the 3d orbital in Cu so that Cu has completely filled $3d^{10}$ orbital, thus acquiring more stability.

***Q.9. Why chromium has electronic configuration $3d^5\ 4s^1$ and not $3d^4\ 4s^2$?**

Ans: Chromium has atomic number 24. Its expected and actual electronic configurations are:

$_{24}$Cr (Expected): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^4\ 4s^2}$

(Actual): $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{3d^5\ 4s^1}$

Explanation:

i. The energy difference between the 3d and 4s orbitals is very low.

ii. The d-orbital being degenerate, acquires more stability when it is half-filled ($3d^5$) or completely filled ($3d^{10}$).

iii. Electron – electron repulsion results in transfer of one electron from 4s orbital to 3d orbital of Cr. This results in half filled $3d^5$ orbital which in turn results in extra stability.

8.2 Occurrences and general characteristics of transition elements

Q.10. State the general characteristics of transition elements or d-block elements. OR
What are the characteristics of the transition elements? (NCERT)

Ans: Characteristics of transition elements:

i. Most of the transition elements are metals and thereby they show metallic properties such as ductility, malleability, electrical conductivity, high tensile strength and metallic lustre.

ii. Except mercury which is liquid at room temperature, other transition elements have typical metallic structures.

iii. Their compounds generally contain unpaired electrons, hence they are paramagnetic in nature and form coloured compounds.

iv. They show variable oxidation states.

v. They have tendency to form large number of complexes.

vi. They have higher densities as compared to the metals of groups 1 and 2 (s-block).

vii. They are heavy metals with higher melting and boiling point as well as higher heats of vaporisation.

viii. Transition elements are less reactive than s-block elements due to their higher ionisation energy.

ix. Most of the transition metals such as Mn, Ni, Co, Cr, V, Pt, etc., and their compounds are used as catalysts.

x. They have good thermal and electrical conductivity.

xi. They form alloys with different metals.

xii. They form interstitial compounds with elements such as hydrogen, boron, carbon, nitrogen, etc.

xiii. They form organometallic compounds.

Q.11. Why do transition metals possess high density and high melting and boiling points?

Ans: i. The densities of d-block elements are relatively higher as compared to the s-block elements due to the decrease in the size of the atoms and the consequent increase in the nuclear charge, which results in the compact structure of the elements.

ii. The density of the atoms increases with the decrease in the size of the atom. Therefore the density of the elements increases from left to right across a period.

iii. Transition elements form strong metallic bond in which both (n–1) d and ns electrons take part.

iv. Due to the notable covalent character of the strong metallic bond, considerable amount of energy is required to break the metallic bond in order to melt the metal. Hence, these metals possess high melting and boiling points.

Q.12. All d-block elements are not transition elements. Explain. OR
Which of the d-block elements may not be regarded as the transition elements? (NCERT)

Ans: i. The d-block elements are those in which the last electron enters the d-orbital.

ii. The transition elements are those elements which have incompletely filled (partly filled) d-subshells in their elementary state or in any one of their oxidation states.

iii. Hence, only those d-block elements which have completely filled d-orbitals, $(n-1)d^{10}$ are not transition elements.

eg. Zn, Cd and Hg atoms have completely filled d-orbitals ($3d^{10}$) in their ground state as well as in their oxidation states. Hence they are d-block elements, but not transition elements.

8.3 General trends in properties of the first row transition elements

Q.13. Explain the metallic characters of the d-block elements.

Ans: i. All the transition elements are metallic in nature. They either have hexagonal close pack (hcp), cubic close pack (ccp) or body centred cubic lattices which is a characteristic of true metal.

ii. They are hard, lustrous, malleable and ductile with high melting and boiling points, and having good thermal and electrical conductivities.

iii. Low ionization enthalpies and presence of vacant orbitals in the outermost shell results in metallic character due to formation of metallic bonds.

iv. In addition to the electrons from outermost energy level, the unpaired d-electrons also contribute for the bond formation. So, greater the number of unpaired d-electrons, stronger is the bonding. This is due to the formation of covalent bonds by the overlapping of the d-orbitals containing unpaired electrons.

Q.14. Why are Cr, Mo and W hard metals while Zn, Cd and Hg are not very hard metals?

Ans: i. The d-orbitals containing unpaired electrons may overlap to form covalent bonds which are responsible for the hardness.

ii. As the number of unpaired electrons increases, the number of covalent bonds and the strength of the metallic bonds increases. The increase in the number of covalent bonds result in increase in the strength and hardness of metal.

iii. Cr, Mo and W have maximum number of unpaired d-electrons which makes them very hard due to increase in the number of covalent bonds.

iv. Zn, Cd, and Hg on the other hand do not have unpaired d-electrons. Hence, they are not very hard.

Q.15. Explain the trends in melting and boiling points of first row transition metals.

Ans: i. Transition metals have hcp, ccp or bcc lattices. They are held together by strong metallic bonds with significant covalent character.

ii. To melt the metal, metallic bonds should be broken. This requires significant energy. Hence transition metals have very high melting and boiling points. The strength of metallic bonds, the melting and boiling points increases with increase in the number of unpaired electrons.

iii. In a given period of transition elements, the number of unpaired electrons in (n−1) d-orbital increases upto d^5 configuration. This results in increase in the strength of metallic bonds and the melting and boiling points.

iv. Pairing of electrons results in decrease in the number of unpaired electrons from d^6 to d^9 configuration. This decreases the strength of metallic bonds and results in progressive decrease in the melting and boiling points, after the middle of the series.

In the first transition series, the number of unpaired electrons increases from Sc to Cr and then decreases. Thus, the strength of metallic bonds and the melting and boiling points increases from Sc to Cr and then decreases.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Outer electronic configuration	$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
No. of unpaired electrons	1	2	3	6	5	4	3	2	1	0

Note: i. Zn, Cd, and Hg do not have unpaired d-electrons. Hence, they are soft and have low melting and boiling points. Mercury (Hg) is liquid at room temperature (melting point 234 K).

ii. Mn and Tc have unexpectedly lower melting points due to complicated lattice structure. They have low enthalpies of atomization.

iii. Osmium (Os) has the highest density (22.6 g cm^{-3}) whereas scandium (Sc) has the lowest (2.99 g cm^{-3}) and is the lightest transition element.

Q.16. Explain the trends observed in the ionization enthalpies of the d-block elements.

Ans: i. The ionization enthalpies of transition elements are higher than the ionization enthalpies of s-block elements and lower than the ionization enthalpies of p-block elements. This is due to the trends in atomic radii and nuclear charge.

ii. The atomic radii of transition elements are lower than the atomic radii of s-block elements and higher than the atomic radii of p-block elements.

iii. The nuclear charges of transition elements are higher than the nuclear charges of s-block elements and lower than the nuclear charges of p-block elements.

iv. As the atomic number increases across a transition series, the first ionization energy increases with some irregularities.

The irregularities are due to shielding of the valence electrons from the nucleus by the added (n−1) d-electrons. Thus, the effect of increased nuclear charge is opposed by the screening effect.

v. The increasing order of the first ionization enthalpies of elements is:

First transition series < second transition series < third transition series

The third transition series comprises of elements having atoms which possess filled 4f-orbitals. On account of the peculiar diffused shape of 4f-orbitals, they exhibit poor shielding. Thus, the valence electrons experience greater nuclear attraction.

vi. As a result, greater amount of energy is required to ionise the elements of the third transition series. Thus, the ionization enthalpies of the third transition series elements are much higher than those of the first and second series.

Q.17. Explain thermodynamic stability of transition metal compounds on the basis of ionization enthalpy.

Ans: i. The thermodynamic stability of transition metal compounds can be predicted on the basis of their ionization enthalpy value.

ii. When the sum of the ionization enthalpies required to attain a particular oxidation state of transition metal ions is small, the thermodynamic stability of the compounds of the metal in that oxidation state is high.

eg.

a. Compounds containing Ni (II) are more stable than compounds containing Pt (II). Less amount of energy is required for the ionization of Ni to Ni^{2+}, than the energy required for the ionization of Pt to Pt^{2+}. This is because the sum of first and second ionization enthalpies ($IE_1 + IE_2$) for nickel is lesser as compared to that of platinum.

$Ni \longrightarrow Ni^{2+}$ ($IE_1 + IE_2 = 2.49 \times 10^3$ kJ mol^{-1})

$Pt \longrightarrow Pt^{2+}$ ($IE_1 + IE_2 = 2.66 \times 10^3$ kJ mol^{-1})

b. Compounds containing Pt (IV) are more stable than compounds containing Ni (IV). Less amount of energy is required for the ionization of Pt to Pt^{4+} than the energy required for the ionization of Ni to Ni^{4+}. This is because the sum of first four ionization enthalpies ($IE_1 + IE_2 + IE_3 + IE_4$) for platinum is lesser as compared to that of nickel.

$Ni \longrightarrow Ni^{4+}$ ($IE_1 + IE_2 + IE_3 + IE_4 = 11.29 \times 10^3$ kJ mol^{-1})

$Pt \longrightarrow Pt^{4+}$ ($IE_1 + IE_2 + IE_3 + IE_4 = 9.36 \times 10^3$ kJ mol^{-1})

Note: K_2PtCl_6 is a well known compound of Pt (IV). The corresponding compound of nickel is not known.

***Q.18. Explain the oxidation states of first row elements of transition series.**

Ans: i. Transition elements have variable oxidation states as both (n −1)d and ns electrons participate in bonding, due to nearly same energy levels.

ii. Elements of first transition series show +1 and +2 as the lowest oxidation states due to presence of 4s electrons.

iii. As the 3d electrons take part in the chemical bonding one after another, there are number of other oxidation states as illustrated below.

Oxidation states of first transition (3d) series elements:

Sc ($3d^1 4s^2$)	Ti ($3d^2 4s^2$)	V ($3d^3 4s^2$)	Cr ($3d^5 4s^1$)	Mn ($3d^5 4s^2$)	Fe ($3d^6 4s^2$)	Co ($3d^7 4s^2$)	Ni ($3d^8 4s^2$)	Cu ($3d^{10} 4s^1$)	Zn ($3d^{10} 4s^2$)
+2	+2	+2	+1	+2	+2	+2	+2	+1	+2
+3	+3	+3	+2	+3	+3	+3	+3	+2	
	+4	+4	+3	+4	+4	+4	+4		
		+5	+4	+5	+5	+5			
			+5	+6	+6				
			+6	+7					

iv. The common oxidation states are +2 and +3.

v. The number of oxidation states increases with increase in the number of unpaired 3d electrons.

Q.19. Compare the stability of +2 oxidation state for the elements of the first transition series. (NCERT)

Ans: i. In the beginning of 3d transition series, Sc^{2+} is virtually not known or in other words it is not stable in comparison to Sc^{3+}. Ti^{2+}, V^{2+}, Cr^{2+} are known but less stable in comparison to their most common oxidation state of +3.

ii. In the middle of the 3d transition series, Mn^{2+}, Fe^{2+}, Co^{2+} are known and quite common. Mn^{2+} and Mn^{7+} are most stable in Mn. Fe^{2+} is less stable in comparison to Fe^{3+}, due to fact that Fe^{2+} tends to lose one electron to acquire d^5 structure, which has extra stability.

iii. Co^{2+} is less stable as compared to Co^{3+}. Ni^{2+} is most common and most stable among its +2, +3 and +4 states. Cu^{+} is more stable and is most common species as compared to Cu^{2+}.

iv. At the end of the 3d transition series, Zn forms only Zn^{2+} which is highly stable as it has $3d^{10}$ configuration.

Q.20. Write the different oxidation states of manganese. Why +2 oxidation state of manganese is more stable? [Mar 13] OR

Explain why Mn^{2+} ion is more stable than Mn^{3+}? (Given: Mn $\rightarrow$ Z = 25) [Mar 14]

Ans: i. Oxidation states of Mn: +2, +3, +4, +5, +6 and +7.

ii. Electronic configuration of Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^0$

Due to the presence of half filled 'd' orbital, the +2 oxidation state of manganese is more stable.

*[**Mar 13**: Oxidation states – **1 Mark**, Electronic configuration – **1 Mark**, Explanation – **1 Mark; Mar 14**: Electronic configuration – **½ Mark**, Explanation – **½ Mark**]*

Q.21. Write the different oxidation states of iron. Why +2 oxidation state of manganese is more stable? (Z of Mn = 25). [Mar 17]

Ans: i. Oxidation states of Fe: +2, +3, +4, +5 and +6. *[Oxidation states – **1 Mark**]*

ii. Electronic configuration of Mn^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^0$ *[Electronic configuration – **1 Mark**]*

Due to the presence of half filled 'd' orbital, the +2 oxidation state of manganese is more stable.

*[Explanation – **1 Mark**]*

Q.22. What is the position of iron (Z = 26) in periodic table? Explain why is Fe^{3+} more stable than Fe^{2+}? [Oct 15]

Ans: i. Iron (Fe) is placed in the 4th period and group 8 of the modern periodic table. *[Explanation – **1 Mark**]*

ii. Electronic configuration of Fe^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ *[Electronic configuration – **½ Mark**]*

iii. Electronic configuration of Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$ *[Electronic configuration – **½ Mark**]*

Due to the presence of half filled 'd' orbital, Fe^{3+} is more stable than Fe^{2+}. *[Explanation – **1 Mark**]*

Q.23. Why does scandium show only +2 and +3 oxidation states?

Ans: i. Scandium (Sc) has electronic configuration, Sc: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

ii. Due to the loss of two electrons from the 4s-orbital, Sc acquires +2 oxidation state.
Sc^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$

iii. By the loss of one more electron from the 3d-orbital, it acquires +3 oxidation state.
Sc^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6$

iv. Since Sc^{3+} acquires extra stability of inert element [Ar], it does not form higher oxidation state.