
Chapter – 8 (The d and f – Block Elements)

Exercise Questions:

Question: 1 Write down the electronic configuration of:

- i.) Cr^{3+}
- ii.) Pm^{3+}
- iii.) Cu^+
- iv.) Ce^{4+}
- v.) Co^{2+}
- vi.) Lu^{2+}
- vii.) Mn^{2+}
- viii.) Th^{4+}

Answer:

- i.) $\text{Cr}^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
Or $[\text{Ar}]^{18} 3d^3$
- ii.) $\text{Pm}^{3+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^4$
Or $[\text{Xe}]^{54} 3d^3$
- iii.) $\text{Cu}^+ : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
Or $[\text{Ar}]^{18} 3d^{10}$
- iv.) $\text{Ce}^{4+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$
Or $[\text{Xe}]^{54}$
- v.) $\text{Co}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$
Or $[\text{Ar}]^{18} 3d^7$
- vi.) $\text{Lu}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^1$
Or $[\text{Xe}]^{54} 4f^{14} 5d^1$
- vii.) $\text{Mn}^{2+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$
Or $[\text{Ar}]^{18} 3d^5$
- viii.) $\text{Th}^{4+} : 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^6$
Or $[\text{Rn}]^{86}$

Question: 2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

Answer:

Mn^{2+} has stable half filled electronic configuration, therefore Mn^{2+} compounds are more stable than Fe^{2+} compounds to their +3 state. Fe^{2+} ($3d^6$) can easily lose one electron to give stable Fe^{3+} ($3d^5$ stable configuration).

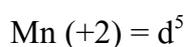
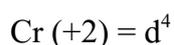
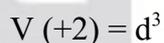
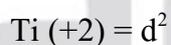
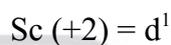
Question: 3 Explain briefly how +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number?

Answer:

The oxidation displayed by the first half of the first row of transition elements is given as:

METALS	Sc[Ar] $3d^14s^2$	Ti[Ar] $3d^24s^2$	V[Ar] $3d^34s^2$	Cr[Ar] $3d^54s^1$	Mn[Ar] $3d^54s^2$
OXIDATION STATES		+2	+2	+2	+2
	+3	+3	+3	+3	+3
		+4	+4	+4	+4
			+5	+5	+6
				+6	+7

It can be easily observed that except Sc, all others metals display +2 oxidation state. Also, on moving from Sc to Mn, the atomic number increases from 21 to 25. This means the number of electrons in the 3d-orbital also increases from 1 to 5.



+2 oxidation state is attained by the loss of the two 4s electrons by these metals. Since the number of d electrons in (+2) state also increases from $Ti(+2)$ to $Mn(+2)$, the stability of

+2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d⁵ electrons (that is half-filled d shell, which is highly stable)

Question: 4 To what extent do the electronic configuration decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

Answer:

The elements in the first half of the transition series exhibit many oxidation states with Mn exhibiting maximum no. of oxidation state (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic no. this happens as more electrons are getting filled in the d orbital. However, Sc does not show +2 oxidation state. Its electronic configuration is 4s²3d¹. It loses all the 3 electrons to form Sc³⁺. +3 oxidation state of Sc is very stable as by losing all three electrons, it attains stable noble gas configuration, [Ar]. Ti(+4) and V(5) are very stable for the same reason. For Mn, +2 oxidation state is very stable as after losing two electrons, its d orbital is exactly half filled, [Ar]3d⁵.

Question: 5 What may be the stable oxidation state of the transition element with the following d elements d electron configuration in the ground state of their atoms.

Answer:

Electronic configuration in ground state	Stable oxidation state
3d ³ (Vanadium)	+2, +3, +4, +5
3d ⁵ (chromium)	+3, +4, +6
3d ⁵ (Manganese)	+2, +4, +6, +7
3d ⁸ (cobalt)	+2, +3
3d ⁴	There is no 3d ⁴ configuration in ground state

Question: 6 Name the oxometal anions of the first series of the transition element with the following d electron configurations in the ground state of their atoms: 3d³, 3d⁵, 3d⁸ and 3d⁴?

Answer:

Name of oxometal anion	Name of metal with oxidation state	Group no. to which metal belong
CrO ₄ ²⁻	Cr in +6 state of oxidation	6 th group
MnO ₄ ⁻	Mn in +7 state	7 th group
Vanadate	Oxidation state +5	

Question: 7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Answer:

The steady decrease in the size of lanthanoid ions (M^{3+}) with the increase in atomic number is called lanthanoid contraction.

Consequences of lanthanoid contraction :

Due to lanthanoid contraction, the size of M^{3+} ions decreases and there is increase in the covalent character in M - OH bond.

Question: 8 In what way is the electronic configuration of the transition elements different from that of the non transition elements?

Answer:

Transition elements have partially filled d orbital but the non transition elements have no d orbital or have completely filled d orbitals.

Question: 9 What are the characteristics of the transition elements and why are they called transition elements? Which of the d block element may not be regarded as the transition element?

Answer:

Transition elements are those elements in which the atoms or ions (in stable oxidation state) contain partially filled d-orbital. These elements lie in the d-block and show a transition of properties between s-block and p-block. Therefore, these are called transition elements.

Elements such as Zn, Cd, and Hg cannot be classified as transition elements because these have completely filled d-subshell.

Question:10 What are the different oxidation states exhibited by the lanthanoids?

Answer:

The most common oxidation state shown by the lanthanoids is +3. In some exceptional cases it may be +2 or +4 (+2 in Eu and Yb and +4 in Ce) in solution and solid compound.

Question:11 Explain giving reasons:

i.)

ii.)

- iii.) **Transition metals and many of their compounds show paramagnetic behaviour.**
- iv.) **The enthalpies of atomisation of the transition metals are high.**
- v.) **The transition metals generally form coloured compounds.**
- vi.) **Transition metals and their many compounds act as good catalyst.**

Answer:

i.) Transition metals show paramagnetic behaviour. Paramagnetism arises due to the presence of unpaired electrons with each electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. However, in the first transition series, the orbital angular momentum is quenched. Therefore, the resulting paramagnetism is only because of the unpaired electron.

(ii) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds. As a result, the enthalpy of atomization of transition metals is high.

(iii) Most of the complexes of transition metals are coloured. This is because of the absorption of radiation from visible light region to promote an electron from one of the d-orbitals to another. In the presence of ligands, the d-orbitals split up into two sets of orbitals having different energies. Therefore, the transition of electrons can take place from one set to another. The energy required for these transitions is quite small and falls in the visible region of radiation. The ions of transition metals absorb the radiation of a particular wavelength and the rest is reflected, imparting colour to the solution.

(iv) The catalytic activity of the transition elements can be explained by two basic facts.

(a) Owing to their ability to show variable oxidation states and form complexes, transition metals form unstable intermediate compounds. Thus, they provide a new path with lower activation energy, E_a , for the reaction.

(b) Transition metals also provide a suitable surface for the reactions to occur.

Question:12 What are the interstitial compounds? Why are such compounds well known for transition metals?

Answer:

The compounds formed when small atoms of H, C or N get trapped inside the crystal lattice of metals is known as interstitial compounds. A number of interstitial compounds are formed by the transition

metals. As vacant spaces of the transition metals are filled up by small atoms, these compounds are hard and rigid.

Interstitial compounds are well known for transition compounds due to its closed crystalline structure with voids in them. The atomic size of transition metals are very large hence have large voids to occupy these small atoms.

Question:13 How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with example.

Answer:

The non-transition elements also show variable oxidation states. However these differ from the variable oxidation states shown by transition elements. Variable oxidation states shown by transition elements can differ by one unit while the oxidation states shown by non-transition elements differ by 2 unit due to inert pair effect. For example, thallium exhibits oxidation states +1, +3 and lead exhibits +2, +4 oxidation states. Moreover, in case of transition elements of the same group, higher oxidation state is more stable for heavier elements. e.g., Mo (VI) and W (VI) are more stable than Cr (VI). In non-transition elements of p-block, lower oxidation state is more stable due to inert pair effect e.g., Pb^{2+} is more stable than Pb^{4+} .

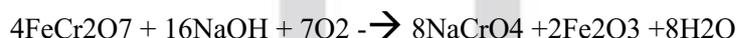
Question:14 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

Answer:

Potassium dichromate is prepared from chromate in the following steps:

Step 1:

Preparation of sodium chromate



Step 2:

Conversion of sodium chromate into sodium dichromate



Step 3:

Conversion of sodium dichromate to potassium dichromate



Potassium dichromate being less soluble than the sodium chloride is obtained in the form of crystals and can be removed.

The dichromate ion exist in equilibrium with chromate ion at pH and however, by changing the pH, they can be interconverted.

Question: 15 Describe the oxidising action of potassium dichromate and write the ionic equation for its reaction with:

- i.) Iodide
- ii.) Iron solution
- iii.) H₂S

Answer:

K₂Cr₂O₇, act as a very strong oxidising agent in the acidic medium.



K₂Cr₂O₇ takes up electrons to get reduced and act as an oxidising agent. The reaction of K₂Cr₂O₇ with the other iodide, iron solution, and H₂S are given below:

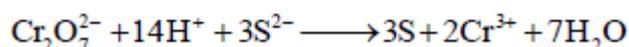
- I.) K₂Cr₂O₇ oxidizes with iodide to iodine



- ii. It oxidizes iron (II) salt to iron (III) salt.



- iii. It oxidizes H₂S to S.



Question:16 For M²⁺/M and M³⁺/M²⁺ systems the E° values for some metal ions are as follows;

Cr ²⁺ /Cr	-0.9V	Cr ³⁺ /Cr ²⁺	-0.4V
Mn ²⁺ /Mn	-1.2V	Mn ³⁺ /Mn ²⁺	+1.5V
Fe ²⁺ /Fe	-0.4V	Fe ³⁺ /Fe ²⁺	+0.8V

Using this data to comment upon:

- i.) The stability of Fe³⁺ in acid solution as to compared that of Mn²⁺ or Cr³⁺ and
- ii.) The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

Answer:

The value for Fe³⁺/Fe²⁺ is higher than that for Cr³⁺/Cr²⁺ and lower than that for Mn³⁺/Mn²⁺. So, the reduction of Fe³⁺ to Fe²⁺ is easier than the reduction of Mn³⁺ to Mn²⁺, but not as easy as the reduction of Cr³⁺ to Cr²⁺. Hence, Fe³⁺ is more stable than Mn³⁺, but less stable than Cr³⁺. These metal ions can be arranged in the increasing order of their stability as:



(ii) The reduction potentials for the given pairs increase in the following order. Mn

$2+/ \text{Mn} < \text{Cr}^{2+}/ \text{Cr} < \text{Fe}^{2+}/ \text{Fe}$, the oxidation of Fe to Fe^{2+} is not as easy as the oxidation of Cr to Cr^{2+} and the oxidation of Mn to Mn^{2+} . Thus, these metals can be arranged in the increasing order of their ability to get oxidised as: $\text{Fe} < \text{Cr} < \text{Mn}$.

Question:17 Predict which of the following will be coloured in aqueous solution?

Ti^{3+} , V^{3+} , Cu^{+} , Sc^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} . Give reason for each.

Answer:

$\text{Ti}^{3+}(3d^1)$, $\text{Fe}^{3+}(3d^5)$, $\text{Mn}^{2+}(3d^5)$, $\text{Co}^{2+}(3d^8)$.

These elements are coloured in aqueous solution because of partially filled d orbitals. Remaining have filled d orbitals, so they are colourless in aqueous solution.

Question:18 Compare the stability of +2 oxidation state for the elements of the first transition series.

Answer:

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

From the above table it is shown that maximum oxidation state are shown by Mn which is from +2 to +7. The no. of oxidation state increases on moving from Sc to Mn. On moving from Mn to Zn, the oxidation state decreases due to decrease in the available no. of unpaired electrons. The relative stability of +2 oxidation state increases from top to bottom. This is because on moving from top to bottom it is more and more difficult to remove third electron from the d orbital.

Question:19 Compare the chemistry of actinoids with that of lanthanoids with special reference to:

- i.) **Electronic configuration**
- ii.) **Atomic and ionic sizes**
- iii.) **Oxidation state**

iv.) Chemical reactivity.

Answer:

Characteristics	Lanthanoids	Actinoids
Electronic configuration	It may be represented by $[Xe]4f^{0-14}5d^0 \text{ or } 16s^2$	It may be represented by $[Rn]5f^{0-14}6d^{0-1}7s^2$
Oxidation state	Show +3 oxidation state only, except in few cases where it is +2 or +4. They never show more than +4 oxidation state.	Show higher oxidation states such as +4, +5, +6, +7 also in addition to +3 oxidation state.
Atomic and ionic sizes	The ionic radii of M^{3+} ions in lanthanoids series show a regular decrease in size of ions with increase in atomic no. this decrease is known as lanthanoid contraction.	There is a greater and gradual decrease in the size of atoms or Mn^{3+} ions across the series. This greater decrease is known as actinoid contraction
Chemical reactivity	These are less reactive metals and form oxides, sulphides, nitrides, hydroxides and halides etc. these also form H_2 with acids. They show a lesser tendency to form a complex.	These are lightly reactive metals especially in finally divided a state. They form a mixture of oxides and hydride by action of boiling water. They combine with non metals even at moderate temperature. They show a greater tendency for complex formation.

Question:20 How would you account for the following:

- i.) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidising.**
- ii.) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagent it is easily oxidised.**
- iii.) The d^1 configuration is very unstable in ions.**

Answer:

(i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as $t^3e^0g^0$ configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and is highly stable.

(ii) $Co(II)$ is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to $Co(III)$. Although the 3rd ionization energy for Co is high, but the higher amount of

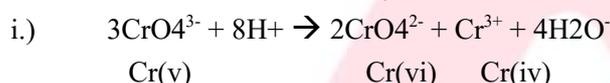
crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.

(iii) The ions in d1 configuration tend to lose one more electron to get into stable d0 configuration. Also, the hydration or lattice energy is more than sufficient to remove the only electron present in the d-orbital of these ions. Therefore, they act as reducing agents.

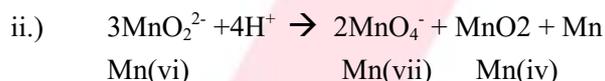
Question:21 What is meant by disproportionation? Give two example of disproportionation reaction in aqueous solution.

Answer:

It is found that sometimes a relatively less stable oxidation state undergoes an oxidation reduction reaction in which it is simultaneously oxidised and reduced. This is called disproportion. For example:



Cr(v) is oxidised to Cr(vi) and reduced to Cr(iv)



Mn (vi) is oxidised to Mn (vii) and reduced to Mn(iv)

Question:22 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Answer:

Cu metal in the first transition series (3d series) shows +1 oxidation state most frequently. This is because the electronic configuration of Cu is $3d^{10}4s^1$ and after losing one electron, it acquires the stable $3d^{10}$ fully filled electronic configuration.

Question:23 Calculate the no. of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution.

Answer:

gaseous ion	electronic config.	No. of unpaired electrons
Mn^{3+}	$[\text{Ar}] 3d^4$	4
Cr^{3+}	$[\text{Ar}] 3d^3$	3
V^{3+}	$[\text{Ar}] 3d^2$	2
Ti^{3+}	$[\text{Ar}] 3d^1$	1

Cr^{3+} is the most stable in aqueous solutions owing to t^3g^2 configuration.

Question:24 Give examples and suggest reason for the following features of transition metal chemistry:

- I.) The lowest oxides of transition metal is basic, the highest is acidic/amphoteric.**
- II.) A transition metal exhibits the highest oxidation state in oxides and fluorides.**
- iii.) The highest oxidation state is exhibited in oxoanions of a metal.**

Answer:

(i) In the case of a lower oxide of a transition metal, the metal atom has a low oxidation state. This means that some of the valence electrons of the metal atom are not involved in bonding. As a result, it can donate electrons and behave as a base.

On the other hand, in the case of a higher oxide of a transition metal, the metal atom has a high oxidation state. This means that the valence electrons are involved in bonding and so, they are unavailable. There is also a high effective nuclear charge. As a result, it can accept electrons and behave as an acid.

For example, Mn_2O is basic and Mn_2O_7 is acidic.

(ii) Oxygen and fluorine act as strong oxidising agents because of their high electronegativities and small sizes. Hence, they bring out the highest oxidation states from the transition metals. In other words, a transition metal exhibits higher oxidation states in oxides and fluorides. For example, in OsF_6 and V_2O_5 , the oxidation states of Os and V are +6 and +5 respectively.

(iii) Oxygen is a strong oxidising agent due to its high electronegativity and small size. So, oxo-anions of a metal have the highest oxidation state. For example, in MnO_4^- , the oxidation state of Mn is +7.

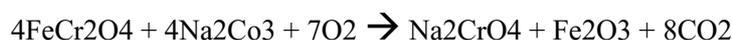
Question:25 Indicate the steps in the preparation of :

- i.) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore**
- ii.) KMnO_4 from pyrolusite ore.**

Answer:

It takes place in three steps:

- i.) Conversion of chromite ore into sodium chromate



- ii.) Conversion of sodium chromate into sodium dichromate
$$2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$$
- iii.) Conversion of sodium dichromate into potassium dichromate.

Question:26 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

Answer:

An alloy is a solid solution of two or more elements in a metallic matrix. It can either be a partial solid solution or a complete solid solution. Alloys are usually found to possess different physical properties than those of the component elements.

An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94-95%), iron (5%), and traces of S, C, Si, Ca, and Al.

Uses

- (1) Mischmetal is used in cigarettes and gas lighters.
- (2) It is used in flame throwing tanks.
- (3) It is used in tracer bullets and shells.

Question:27 What are inner transition elements? Decide which of the following atomic no. are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

Answer:

Inner transition metals are those elements in which the last electron enters the f-orbital. The elements in which the 4f and the 5f orbitals are progressively filled are called f-block elements. Among the given atomic numbers, the atomic numbers of the inner transition elements are 59, 95, and 102.

Question:28 The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

Answer:

Lanthanoids show limited number of oxidation state, viz., +2, +3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f and 5d-subshells. The dominant oxidation state of actinoids is also +3 but they show a number of other oxidation states also. eg. uranium ($Z = 92$) and plutonium ($Z = 94$), show +3, +4, +5 and +6, neptunium ($Z = 93$) shows +3, +4, +5, +6 and +7 etc. This is due to small energy difference between 5f, 6d and 7s-subshells of the actinoids.

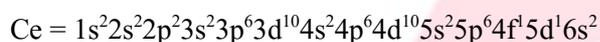
Question:29 Which is the last element in the series of actinoids? Write electronic configuration of this element. Comment on the possible oxidation state of this element.

Answer:

The last element in the actinoid series is lawrencium, Lr. Its atomic number is 103 and its electronic configuration is $[Rn]5f^{14}6d^17s^2$. The most common oxidation state displayed by it is +3; because after losing 3 electrons it attains stable f^{14} configuration.

Question:30 Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

Answer:



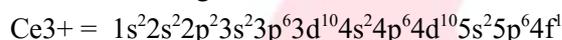
Magnetic moment can be calculated as;

$$u = \sqrt{n(n+2)}$$

Where,

N = no. of unpaired electrons

Electronic configuration of



In Ce^{3+} , $n = 1$

$$\therefore u = \sqrt{1(1+2)} = 1.732 \text{ BM}$$

Question:31 Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.

Answer:

The lanthanides that exhibit +2 and +4 states are shown in the given table. The atomic numbers of the elements are given in the parenthesis.

+2	+4
Nd(60)	Ce(58)
Sm(62)	Pr(59)
Eu(63)	Nd(60)
Tm(69)	Tb(65)
Yb(70)	Dy(66)

Ce after forming Ce^{4+} attains a stable electronic configuration of $[Xe]$.

Tb after forming Tb^{4+} attains a stable electronic configuration of $[Xe] 4f^7$
Eu after forming Eu^{2+} attains a stable electronic configuration of $[Xe] 4f^7$.
Yb after forming Yb^{2+} attains a stable electronic configuration of $[Xe] 4f^{14}$.

Question:32 Compare the chemistry of actinoids with that of lanthanoids with special reference to:

- i.) Electronic configuration**
- ii.) Oxidation state**
- iii.) Chemical reactivity.**

Answer: Check answer 19.

Question:33 Write the electronic configuration of the elements with the atomic numbers 61, 91, 101, 109.

Answer:

Atomic number	Electronic configuration
61	$[Xe]^{54} 4f^5 5d^0 6s^2$
91	$[Rn]^{86} 5f^2 6d^1 7s^2$
101	$[Rn]^{86} 5f^{13} 5d^0 7s^2$
109	$[Rn]^{86} 5f^{14} 6d^7 7s^2$

Question:34 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points.

- I.) Electronic configuration**
- II.) Oxidation state**
- III.) Ionisation enthalpies**
- IV.) Atomic sizes**

Answer:

- i.) In the 1st, 2nd and 3rd transition series, the 3d, 4d and 5d orbitals are respectively filled. We know that elements in the same vertical column generally have similar electronic configurations
- ii.) In each of the three transition series the number of oxidation states shown by the elements is the maximum in the middle and the minimum at the extreme ends. However, +2 and +3

oxidation states are quite stable for all elements present in the first transition series. All metals present in the first transition series form stable compounds in the +2 and +3 oxidation states. The stability of the +2 and +3 oxidation states decreases in the second and the third transition series, wherein higher oxidation states are more important. For example are stable complexes, but no such complexes are known for the second and third transition series such as Mo, W, Rh, In. They form complexes in which their oxidation states are high. For example: WCl_6 , ReF_7 , RuO_4 , etc.

- iii.) In each of the three transition series, the first ionisation enthalpy increases from left to right. However, there are some exceptions. The first ionisation enthalpies of the third transition series are higher than those of the first and second transition series. This occurs due to the poor shielding effect of 4f electrons in the third transition series. Certain elements in the second transition series have higher first ionisation enthalpies than elements corresponding to the same vertical column in the first transition series. There are also elements in the 2nd transition series whose first ionisation enthalpies are lower than those of the elements corresponding to the same vertical column in the 1st transition series.
- iv.) Atomic size generally decreases from left to right across a period. Now, among the three transition series, atomic sizes of the elements in the second transition series are greater than those of the elements corresponding to the same vertical column in the first transition series. However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

Question:35 Write down the number of 3d electrons in each of the following ions: Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions.

Answer:

	Element	Ion	Occupancy of 3d orbitals
a.	$\text{Ti} (Z = 22) = 3d^2 4s^2$	$\text{Ti}^{2+} = 3d^2$	t_{2g}^2
b.	$\text{V} (Z = 23) = 3d^3 4s^2$	$\text{V}^{2+} = 3d^3$	t_{2g}^3
c.	$\text{Cr} (Z = 24) = 3d^5 4s^1$	$\text{Cr}^{3+} = 3d^3$	t_{2g}^3
d.	$\text{Mn} (Z = 25) = 3d^5 4s^2$	$\text{Mn}^{2+} = 3d^5$	t_{2g}^5
e.	$\text{Fe} (Z = 26) = 3d^6 4s^2$	$\text{Fe}^{2+} = 3d^6$	t_{2g}^6
f.	$\text{Fe} (Z = 26) = 3d^6 4s^2$	$\text{Fe}^{3+} = 3d^5$	t_{2g}^5
g.	$\text{Co} (Z = 27) = 3d^7 4s^2$	$\text{Co}^{2+} = 3d^7$	$t_{2g}^6 e_g^1$
h.	$\text{Ni} (Z = 28) = 3d^8 4s^2$	$\text{Ni}^{2+} = 3d^8$	$t_{2g}^6 e_g^2$
i.	$\text{Cu} (Z = 29) = 3d^{10} 4s^1$	$\text{Cu}^{2+} = 3d^9$	$t_{2g}^6 e_g^3$

Question:36 Comment on the statement that elements of the first transition series possesses many properties different from those of heavier transition elements.

Answer:

The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

(ii) +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements.

Question:37 What can be inferred from the magnetic moment values of the following complex species?

Example	Magnetic moment(BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

Answer:

Magnetic moment (u) is given as

$$u = \sqrt{n(n + 2)}$$

$$n = 1, u = 1.732$$

$$n = 2, u = 2.83$$

$$n = 3, u = 3.87$$

$$n = 4, u = 4.899$$

$$n = 5, u = 5.92$$

i.) $K_4[Mn(CN)_6]$

For transition metals, the magnetic moment is calculated from the spin only formula. Therefore

$$\sqrt{n(n + 2)} = 2.2$$

We can see from above calculation that the given value is closet to $n - 1$. Also, in this complex, Mn is the +2 oxidation state. This means that Mn has 5 electrons in d orbital. Hence we can say that CN is a strong ligand that caused the pairing of electrons.

ii.) $[Fe(H_2O)_6]^{2+}$

We can see from the above calculation that magnetic moment is 5.3 is closest to the value when $n = 4$. Also, in this complex, Fe is the +2 oxidation state. This means that Fe has six electrons in the d orbital. Hence, H₂O is a weak field ligand and does not cause the pairing of electrons.

iii.) $K_2[MnCl_4]$

we can see that $x = 5.9$ is closest to the value when $n = 5$. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the d orbital. Hence Cl^- is a weak ligand and does not cause the pairing of electrons.



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