### #420216

Topic: Study of d-Block elements

Choose the correct alternative:

(a) Alloys of metals usually have (greater/less) resistivity than that of their constituent metals.

(b) Alloys usually have much (lower/higher) temperature coefficients of resistance than pure metals.

(c) The resistivity of the alloy manganin is nearly independent of / increases rapidly with increase of temperature.

(d) The resistivity of a typical insulator (e.g., amber) is greater than that of a metal by a factor of the order of  $(10^{22}/10^3)$ .

### Solution

(a) Alloys of metals usually have greater resistivity than that of their constituent metals.

(b) Alloys usually have much lower temperature coefficients of resistance than pure metals.

(c) The resistivity of the alloy manganin is nearly independent of increase of temperature.

(d) The resistivity of a typical insulator is greater than that of a metal by a factor of the order of  $10^{22}$ .

### #457820

Topic: Study of d-Block elements

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)  $Th^{4+}$ 

### Solution

The electronic configurations of various ions are as shown:  $Cr^{3+}$  :  $[Ar]3d^3$   $Pm^{3+}$  :  $[Xe]4f^4$   $Cu^+$  :  $[Ar]3d^{10}$   $Ce^{4+}$  : [Xe] $Co^{2+}$  :  $[Ar]3d^7$ 

 $Lu^{2+}\,:\,[Xe]4f^{14}5d^1 \ Mn^{2+}\,:\,[Ar]3d^5$ 

 $Th^{4+}$  : [Rn]

### #457839

Topic: Study of d-Block elements

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

# Solution

 $Mn^{2+}$  ion has electronic configuration  $[Ar]3d^5$ . 3d orbital is half filled and stable. Due to this, third ionization enthalpy is very high. The removal of third electron is difficult. On the other hand,  $Fe^{2+}$  has electronic configuration  $[Ar]3d^6$ . Loss of one electron results in stable  $[Ar]3d^5$  electronic configuration. In this 3d orbital, orbital will be half filled which leads to stability. Hence, removal of third electron is easy.

#### #457840

Topic: Study of d-Block elements

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

# Solution

+2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number as 3d orbitals acquire only one electron in each of five 3d orbitals (remain half filled) and the electronic repulsion is least and the nuclear charge increases. In second half of the first row transition series, electrons pair up in 3d orbitals. This increases the electronic repulsion.

# #457842

Topic: Study of d-Block elements

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

#### Solution

When d orbitals are half filled or completely filled, the oxidation state is more stable. Thus, Mn (Z=25) has electronic configuration  $[Ar]3d^54s^2$ . +2 oxidation state is most stable as it has stable electronic configuration (half filled 3d orbital). Also, Zn (Z = 30) has electronic configuration  $[Ar]3d^{10}4s^2$ .. +2 oxidation state is most stable as it has stable

electronic configuration (completely filled 3d orbital).

### #457846

# Topic: Study of d-Block elements

What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms:  $3d^3$ ,  $3d^5$ ,  $3d^8$  and  $3d^4$ ?

#### Solution

Up to Mn, the maximum stable oxidation state corresponds to sum of s and d electrons. After Mn, there is decrease in the stability of higher oxidation states. The stable oxidation

states of the transition elements with the following d electron configurations in the ground state of their atoms are as shown.

 $egin{array}{rll} 3d^34s^2&:\,+5\ 3d^54s^1&:\,+1,+6\ 3d^54s^2&:\,+2,\,+7\ 3d^84s^2&:\,+2\ 3d^44s^2&:\,+1,+6 \end{array}$ 

# #457847

Topic: Important compounds of transition elements

Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

### Solution

 $MnO_4^-$ : Mn has +7 oxidation number and group number is 7.  $CrO_4^{2-}$ : Cr has +6 oxidation state and group number is 6.

### #457851

### Topic: Lanthanoids

What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

# Solution

Lanthanoid contraction is the steady decrease in the atomic and ionic sizes of lanthanide elements with increasing atomic number. This decrease is not much and shows some irregularities.

inegularities.

Atomic radii decreases from La (165 pm) to Lu (156 pm).

lonic radii (+3 oxidation state) decreases from  $Ce^{3+}$  (103 pm) to  $Lu^{3+}$  (85 pm). The consequences of lanthanoid contraction are as follows:

(1) Basicity decreases from  $Ce(OH)_3$  to  $Lu(OH)_3$ .

(2) Covalent nature increases from  $Ce(OH)_3$  to  $Lu(OH)_3$ .

(3) Electronegativity for  $M^{3+}$  ion increases.

(4) There is slight increase in  $E^o$  values.

#### #457852

# Topic: Study of d-Block elements

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

#### Solution

The elements in which the atoms or ions contain partly filled d orbitals are called transition elements. They lie in the d-block of periodic table and show a transition of properties

between s-block and p-block elements. Hence, they are called transition elements. Zn Cd and Hg cannot be classified as transition elements as they have completely filled dsubshell.

### #457855

Topic: Study of d-Block elements

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

#### Solution

In transition elements, d orbitals are filled and in representative elements, s and p orbitals are filled. Transition elements have general electronic configuration  $(n-1)d^{1-10}ns^{1-2}$ 

. Representative elements have general electronic configuration  $ns^{1-2}$  or  $ns^2np^{1-6}$ . In representative elements, last shell is incompletely filled and in transition elements, last

two shells are incompletely filled.

### #457856

# Topic: Lanthanoids

What are the different oxidation states exhibited by the lanthanoids?

### Solution

Apart from +3 oxidation state, lanthanoids also show +2 and +4 oxidation states.

#### #457859

Topic: Study of d-Block elements

Explain giving reasons:

(i) Transition metals and many of their compounds show paramagnetic behaviour.

(ii) The enthalpies of atomisation of the transition metals are high.

(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst

#### Solution

(i) Transition metals and many of their compounds show paramagnetic behaviour.

This is due to presence of one or more unpaired electrons in d subshell.

(ii) The enthalpies of atomisation of the transition metals are high.

This is due to high effective nuclear charge and large number of valence electrons. This results in formation of strong metallic bonds.

(iii) The transition metals generally form coloured compounds.

This is due to d-d transition of unpaired electrons. In presence of ligands, the d orbitals split into two sets. Transition metal ions absorb radiation of a particular wavelength and reflect the remaining. This imparts colour.

(iv) Transition metals and their many compounds act as good catalyst.

Transition metals show variable oxidation states and forms complexes. They form unstable intermediate compounds. They provide a new path with lower activation energy of reaction. They also provide a suitable surface for the reaction to occur.

### #457860

Topic: Study of d-Block elements

What are interstitial compounds? Why are such compounds well known for transition metals?

### Solution

Transition elements have large atomic size and have several interstitial sites. They can trap atoms (having small atomic size such as H, C, N) of other elements in the interstitial

sites of crystal lattice to form interstitial compounds.

### #457862

Topic: Study of d-Block elements

How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples

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In case of transition elements, the variability in the oxidation state is due to participation of (n-1) d orbitals and ns orbitals. The oxidation states differ by unity. Thus, V shows

+2, +3, +4 and +5 oxidation states and Mn shows +2, +3, +4, +5, +6 and +7 oxidation states. On the other hand, the variable oxidation states shown by some p block

elements differ by two units. Thus, tin shows +2 and +4 oxidation state and indium shows +1 and +3 oxidation states.

#### #457863

Topic: Important compounds of transition elements

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

#### Solution

Preparation of potassium dichromate  $K_2Cr_2O_7$  from chromite ore  $FeO \cdot Cr_2O_3(FeCr_2O_4)$ : (i) Chromite ore is fused with NaOH or sodium carbonate in air to form sodium chromate.  $4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$ 

(ii) Sodium chromate solution is filtered and acidified to form sodium dichromate

 $2Na_2CrO_4 + H_2SO_4 
ightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O_7$ 

The solution is cooled to remove crystallized sodium sulphate. Sodium dichromate remains soluble.

(iii) Equimolar proportions of a hot solution of sodium dichromate and KCI are mixed to form potassium dichromate.

 $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ 

Sodium chloride precipitates out in hot solution and is removed by filtration. On cooling, potassium dichromate separates out from the mother liquor.

At pH 4, there is an equilibrium between chromate ions and dichromate ions

 $Cr_2O_7^{2-}$  +  $H_2O \Longrightarrow 2CrO_4^{2-}$  +  $2H^+$ Dichromate ion (orange red) Chromate ion (yellow)

By adding alkali, pH can be increased and the equilibrium reaction will shift in the forward direction to produce more chromate ions (yellow color). This is in accordance with Le chatelier's principle. By adding an acid, pH can be decreased and the equilibrium reaction will shift in the backward direction to produce more dichromate ions (orange-red color).

# #457865

Topic: Important compounds of transition elements

Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii)  $H_2S$ 

### Solution

Potassium dichromate is powerful oxidizing agent in acidic medium. In presence of dilute sulphuric acid, it liberates nascent oxygen.

 $K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$ 

In acidic medium, dichromate ion takes up electrons and acts as oxidizing agent.

 $Cr_2O_7^{2-} + 14H^+ + 6e^- o 2Cr^{3+} + 7H_2O$ 

The net ionic equations for its reaction with (i) iodide (ii) iron(II) solution and (iii)  $H_2S$  are as shown below.

 $Cr_2O_7^{2-}+6I^-+14H^+ 
ightarrow 2Cr^{3+}+3I_2+7H_2O$ 

 $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+}6Fe^{3+} + 7H_2O$  $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{3+} + 3S + 7H_2O$ 

### #457866

Topic: Important compounds of transition elements

Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO2 and (iii) oxalic acid? Write the ionic

equations for the reactions.

Preparation of potassium permanganate,  $KMnO_4$  from pyrolusite ore  $MnO_2$ .

(i) Pyrolusite ore is fused with KOH (or K2CO3) in presence of air (or oxidising agents such as KNO3 or KClO3) to give potassium manganate K2MnO4 (green mass).

$$2MNO_2 + 4KOH + O_2 \xrightarrow{Delta} 2K_2MnO_4 + 2H_2O$$

(ii) Extraction of green mass with water followed by oxidation with chlorine (or ozone or  $CO_2$ ) gives potassium permanganate.

 $2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$ 

On concentrating the solution, dark purple crystals of potassium permanganate separates out.

Note: In neutral or acidic medium, manganate ion will disproportionate to permanganate ion.

 $3MnO_4^{2-} + 4H^+ 
ightarrow 2MnO_4^- + MnO_2 + 2H_2O$ 

Convertion of manganate to permanganate can also be carried by electrolytic oxidation.

Reactions of acidified permanganate solution with (i) iron(II) ions (ii)  $SO_2$  and (iii) oxalic acid:

 $2MnO_4^- + 10Fe^{2+} + 16H^+ \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O$ 

 $2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$ 

 $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ 
ightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ 

### #457875

Topic: Study of d-Block elements

For  $M^{2+}/M$  and  $M^{3+}/M^{2+}$  systems the  $E^{\ominus}$  values for some metals 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

Use this data to comment upon:

(i) the stability of  $Fe^{3+}$  in acid solution as compared to that of  $Cr^{3+}$  or  $Mn^{3+}$  and

(ii) the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal

### Solution

(a) The reduction potential of  $Cr^{3+}/Cr^{2+}$  is negative and hence, Cr(III) is most stable as it cannot be reduced to Cr(II).

 $Mn^{3+}/Mn^{2+}$  has large positive value and Mn(III) is least stable as it can be easily reduced to Mn(II).

 $Fe^{3+}/Fe^{2+}$  has small positive value and Fe(III) is more stable than Mn(III) but less stable than Cr(III).

(b)  $Mn^{2+}/Mn$  has most negative reduction potential and it is most easily oxidised. The ease of oxidation is Mn>Cr>Fe

# #457878

Topic: Study of d-Block elements

 $\label{eq:predict} \mbox{ which of the following will be coloured in aqueous solution}? Ti^{3+}, V^{3+}, Cu^+, Sc^{3+}, Mn^{2+}, Fe^{3+} \mbox{ and } Co^{2+}. \mbox{ Give reasons for each of the solution} \mbox{ and } Sc^{3+}, Mn^{2+}, Fe^{3+} \mbox{ and } Co^{2+}. \mbox{ and } Co^{$ 

### Solution

Transition metal ions with incompletely filled d orbitals are colored and those with completely filled d orbitals (or vacant d orbitals) are colorless.

 $Ti^{3+}, V^{3+}, Mn^{2+}$  and  $Co^{2+}$  are colored due to d-d transition in incompletely filled d orbitals.

 $Cu^+, Sc^{3+}$  are colorless due to completely filled and empty d orbitals respectively.

#### #457880

Topic: Study of d-Block elements

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

### Solution

The +2 state becomes more and more stable in the first half of the first row transition elements with increasing atomic number as 3d orbitals acquire only one electron in each of five 3d orbitals (remain half filled) and the electronic repulsion is least and the nuclear charge increases. In second half of the first row transition series, electrons pair up in 3d orbitals. This increases the electronic repulsion.

# #457883

Topic: Actinoids

# https://community.toppr.com/content/questions/print/?show\_answer=1&show\_topic=1&show\_solution=1&page=1&qid=457847%2C+4578...

Compare the chemistry of actinoids with that of the lanthanoids with special reference to: (i) electronic configuration (ii) atomic and ionic sizes and (iii) oxidation state (iv) chemical

reactivity

#### Solution

(i) Electronic configuration

lanthanoids have general electronic configuration  $[Xe]4f^{1-14}5d^{0-1}6s^2$ . Actinoids have general electronic configuration  $[Rn]5f^{1-14}6d^{0-1}7s^2$ .

In lanthanoids, 4f orbital is filled and in actinoids, 5f orbital is filled.

(ii) Atomic and ionic sizes

The atomic and ionic sizes of lanthanoids and actinoids decrease with increase in the atomic number due to lanthanoid and actinoid contraction.

(iii) Oxidation state

Apart from +3 oxidation state, lanthanoids show +2 and +4 oxidation states due to large energy gap between 4f and 5d subshells. Whereas actinoids show large number of

oxidation states due to small energy gap between 5f and 6d subshells.

(iv) Chemical reactivity

Highly electropositive lanthanoids have almost similar chemical reactivity. Actinoids (electropostive and highly reactive) are more reactive (specially in finely divided state) than lanthanoids.

### #457886

Topic: Study of d-Block elements

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 reagents it is easily oxidised.

(iii) The  $d^1$  configuration is very unstable in ions

### Solution

(i)  $Cr^{3+}/Cr^{2+}$  has negative value of standard electrode potential (-0.41~V) and  $Mn^{3+}/Mn^{2+}$  have positive value (+1.57 V).  $Cr^{2+}$  can undergo oxidation and acts as reducing

agent.  $Mn^{3+}$  can undergo reduction and is oxidizing agent.

(ii) Co (III) being more stable than Co(II), the change in the oxidation state of cobalt from +2 to +3 is easy in presence of complexing agent.

(iii) Once ns electrons are lost, removal of d<sup>1</sup> electron will result in a stable electronic configuration. Such elements either acts as reducing agents or undergo

disproportionation.

# #457890

Topic: Study of d-Block elements

What is meant by disproportionation? Give two examples of disproportionation reaction in aqueous solution.

#### Solution

In disproportionation reactions, same substance is oxidized as well as reduced. For example,

 $2H_2O_2 o 2H_2O + O_2$  $2MnO_4^{2-} + 4H^+ o MnO_4^- + MnO_2 + 2H_2O$ 

### #457891

Topic: Study of d-Block elements

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

# Solution

Copper metal (with electronic configuration  $[Ar]3d^{10}4s^1$ ) in the first series of transition metals exhibits +1 oxidation state most frequently as it readily loses one electyron

(present in 4s) orbital to give stable  $3d^{10}$  electronic configration.

# #457895

Topic: Study of d-Block elements

Calculate the number 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?

The electronic configuration of various ions are given below:

 $Mn^{3+}~:~3d^4$ , Number of unpaired electrons is 4.

 $Cr^{3+}$  :  $3d^3$ , Number of unpaired electrons is 3.

 $V^{3+}$  :  $3d^2$ , Number of unpaired electrons is 2.

 $Ti^{3+}\,:\,3d^4$ , Number of unpaired electrons is 1.

 ${\cal C}r^{3+}$  is most stable in aqueous solution.

### #457897

Topic: Study of d-Block elements

Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) The highest oxidation state is exhibited in oxoanions of a metal.

#### Solution

(i)  $Mn^{(II)}O$  is basic and  $Mn^{(VII)}_2O_7$  is acidic.

 $Cr^{(II)}O$  is basic and  $Cr^{(III)}_2O_3$  is amphoteric.

The ions in lower oxidation state can readily donate electrons and acts as bases and the ions in high oxidation states have a tendency to accept electrons and act as an acid. (ii) Small sized (and highly electronegative) oxygen and fluorine can readily oxidize the metals. For example,  $Os^{(VI)}F_6$  and  $V_2^{(VI)}O_5$ . (iii) Due to high electronegativity and high oxidizing power of oxygen, metal oxoanions have highest oxidation state. For example, In dichromate ion, Cr has +6 oxidation state and in permanganate ion, Mn has +7 oxidation state.

### #457901

Topic: Important compounds of transition elements

Indicate the steps in the preparation of:

(i)  $K_2 C r_2 O_7$  from chromite ore. (ii)  $K M n O_4$  from pyrolusite ore.

### Solution

Preparation of potassium dichromate  $K_2Cr_2O_7$  from chromite ore  $FeO \cdot Cr_2O_3(FeCr_2O_4)$ :

(i) Chromite ore is fused with NaOH or sodium carbonate in air to form sodium chromate.

 $4FeCr_2O_4+16NaOH+7O_2\rightarrow 8Na_2CrO_4+2Fe_2O_3+8H_2O$ 

(ii) Sodium chromate solution is filtered and acidified to form sodium dichromate.

 $2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ 

The solution is coled to remove crystallized sodium sulphate. Sodium dichromate remains soluble.

(iii) Equimolar proportions of hot solution of sodium dichromate and KCI are mixed to form potassium dichromate.

 $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ 

Sodium chloride precipitates out in hot solution and is removed by filtration. On cooling, potassium dichromate separates out from mother liquor.

Preparation of potassium permanganate  $KMnO_4$  from pyrolusite ore  $MnO_2$  .

(i) Pyrolusite ore is fused with KOH (or  $K_2CO_3$ ) in presence of air (or oxidising agents such as  $KNO_3$  or  $KClO_3$ ) to give potassium manganate  $K_2MnO_4$  (green mass)  $2MNO_2 + 4KOH + O_2 \xrightarrow{Delta} 2K_2MnO_4 + 2H_2O$ 

(ii) Extraction of green mass with water followed by oxidation with chlorine (or ozone or  $CO_2$ ) gives potassium permanganate.

 $2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$ 

On concentrating the solution, dark purple crystals of potassium permanganate separates out.

Note: In neutral or acidic medium, manganate ion will disproportionate to permanganate ion.

 $3MnO_4^{2-}+4H^+
ightarrow 2MnO_{\overline{4}}^-+MnO_2+2H_2O$ 

Convertion of manganate to permanganate can also be carried by electrolytic oxidation.

# #457902

Topic: Lanthanoids

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

#### Solution

An alloy is a homogeneous mixture of two or more metals or metal and nonmetals. Misch metal is an important alloy of lanthanoids. It contains 95% lanthanoid metal and 5% iron and traces of *S*, *C*, *Ca* or *Al*. It is used in the magnesium based alloy to produce bullets, shells and lighter flints.

### #457904

### Topic: Lanthanoids

What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104

### Solution

F block elements are the inner transition elements. Last electron enters f-subshell. These includes lanthanoids (Z = 58-71) and actinoids (Z = 90 - 103). Elements with atomic

numbers 59, 95 and 102 are inner transition elements.

# #457906

### Topic: Actinoids

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

#### Solution

Apart from +3 oxidation state, lanthanoids show +2 and +4 oxidation states due to large energy gap between 4f and 5d subshells. Whereas actinoids show large number of

oxidation states due to small energy gap between 5f and 6d subshells.

For example, uranium (Z = 92) shows +3, +4, +5 and +6 oxidation states and neptunium (Z=94) shows +3,+4,+5,+6 and +7 oxidation states due to small energy gaps between 5f and 6d orbitals.

### #457907

### Topic: Actinoids

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

### Solution

Lawrencium (Z=103) is the last element in the actinoid series. Its electronic configuration is  $[Rn]^{86}5f^{14}6d^{1}7s^{2}$ . Its possible oxidation state is +3.

# #457909

# Topic: Study of d-Block elements

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.

# Solution

 $Ce(Z=58)\,:\,[Xe]^{54}4f^{1}5d^{1}6s^{2}$  $Ce^{3+}\,:\,[Xe]^{54}4f^{1}$ It has 1 unpaired electron.

$$\mu_s = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73$$
B.M

# #457912

# Topic: Lanthanoids

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.

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Ce~(Z = 58),~Pr~(Z = 59),~Nd~(Z = 60),~Tb~(Z = 65) and Dy~(Z = 66) shows +4 oxidation state. They acquire electronic configuration closer to  $4f^0$  and  $4f^7$ . Nd~(Z = 60),~Sm~(Z = 62),~Eu~(Z = 63),~Tm~(Z = 69) and Yb~(Z = 70)\$ shows +2 oxidation state. They acquire half filled  $(4f^7)$  and completely filled  $(4f^{14})$  electronic configurations.

# #457914

# Topic: Actinoids

Compare the chemistry of the actinoids with that of lanthanoids with reference to: (i) electronic configuration (ii) oxidation states and (iii) chemical reactivity

### Solution

(i) Electronic configuration

Lanthanoids have general electronic configuration  $[Xe]4f^{1-14}5d^{0-1}6s^2$ . Actinoids have general electronic configuration  $[Rn]5f^{1-14}6d^{0-1}7s^2$ .

In lanthanoids, 4f orbital is filled and in actiniods, 5f orbital is filled.

(ii) Oxidation state

Apart from +3 oxidation state, lanthanoids show +2 and +4 oxidation states due to large energy gap between 4f and 5d subshells. Whereas actinoids show large number of

oxidation states due to small energy gap between 5f and 6d subshells.

(iii) Chemical reactivity

Highly electropositive lanthanoids have almost similar chemical reactivity. Actinoids (electropostive and highly reactive) are more reactive (specially in finely divided state) than lanthanoids.

# #457915

Topic: Actinoids

Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109

# Solution

$$\begin{split} &Z=61\,:\,[Xe]4f^{5}5d^{0}6s^{2}\\ &Z=91\,:\,[Rn]5f^{2}6d^{1}7s^{2}\\ &Z=101\,:\,[Rn]5f^{13}6d^{0}7s^{2}\\ &Z=109\,:\,[Rn]5f^{14}6d^{7}7s^{2} \end{split}$$

# #457917

Topic: Study of d-Block elements

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 configurations (ii) oxidation states (iii) ionisation enthalpies and (iv) atomic sizes

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# (i) Electronic configuration

In the first transition series, 3d orbitals are progressively filled whereas, in second and third transition series, 4d and 5d orbitals are filled.

### (ii) Oxidation states

+2 and +3 oxidation states of first transition series elements are more stable than +2 and +3 oxidation states of second and third transition series elements. Cobalt forms several complexes with +2 and +3 oxidation states but no such complexes are known for *Rh*, *Ir* which belong to the same group to which *Co* belongs. The maximum oxidation state in a group increases from first transition series to third transition series. In group 8, iron shows +2 and +3 oxidation states and ruthenium and osmium show +4, +6 and +8 oxidation states.

#### (iii) Ionization enthalpies

5d series elements have higher ionization enthalpies than 3d and 4d series elements. In 5d series, 4f orbitals are filled which have poor shielding effect and valence electrons experience higher effective nuclear charge. This results in higher ionization enthalpies for 5d series elements.

### (iv) Atomic sizes

4d series elements have higher atomic size than 3d series elements.

4d and 5d series elements have nearly same atomic size due to lanthanoid contraction.

### #457920

Topic: Study of d-Block elements

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 (octahedral).

### Solution

The number of 3d electrons and the occupancy of 3d orbitals for various transition metal ions are as shown.

 $\begin{array}{l} Ti^{2+}\,:\,3d^2\,:\,t^2_{2g}\,e^0_g\\ V^{2+}\,:\,3d^3\,:\,t^3_{2g}\,e^0_g\\ Cr^{3+}\,:\,3d^3\,:\,t^3_{2g}\,e^0_g\\ Mn^{2+}\,:\,3d^5\,:\,t^3_{2g}\,e^2_g\\ Fe^{2+}\,:\,3d^6\,:\,t^4_{2g}\,e^2_g\\ Fe^{3+}\,:\,3d^5\,:\,t^3_{2g}\,e^2_g\\ Co^{2+}\,:\,3d^7\,:\,t^5_{2g}\,e^2_g\\ Ni^{2+}\,:\,3d^8\,:\,t^6_{2g}\,e^2_g\\ Cu^{2+}\,:\,3d^9\,:\,t^6_{2g}\,e^2_g\\ \end{array}$ 

### #457921

Topic: Study of d-Block elements

Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

# (i) Electronic configurations

In the first transition series, 3d orbitals are progressively filled whereas, in second and third transition series, 4d and 5d orbitals are filled.

### (ii) Oxidation states

+2 and +3 oxidation states of first transition series elements are more stable than +2 and +3 oxidation states of second and third transition series elements. Cobalt forms several complexes with +2 and +3 oxidation states but no such complexes are known for Rh, Ir which belong to the same group to which Co belongs. The maximum oxidation state in a group increases from first transition series to third transition series. In group 8, iron shows +2 and +3 oxidation states and ruthenium and osmium shows +4, +6 and +8 oxidation states.

### (iii) lonization enthalpies

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# (iv) Atomic sizes

4d series elements have higher atomic size than 3d series elements.

4d and 5d series elements have nearly same atomic size due to lanthanoid contraction.