F and D Block Elements VI

NCERT PROBLEMS

Q10 :

Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Answer :

In actinoids, 5*f* orbitals are filled. These 5*f* orbitals have a poorer shielding effect than 4*f* orbitals (in lanthanoids). Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more that that experienced by lanthanoids. Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

Q7 :

What is lanthanoid contraction? What are the consequences of lanthanoid

contraction?

Answer :

As we move along the lanthanoid series, the atomic number increases gradually by one. This means that the number of electrons and protons present in an atom also increases by one. As electrons are being added to the same shell, the effective nuclear charge increases. This happens because the increase in nuclear attraction due to the addition of proton is more pronounced than the increase in the interelectronic repulsions due to the addition of electron. Also, with the increase in atomic number, the number of electrons in the 4*f*orbital also increases. The 4*f*electrons have poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the attraction of the nucleus for the outermost electrons increases. This results in a steady decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.

Q10 :

What are the different oxidation states exhibited by the lanthanoids?

Answer :

In the lanthanide series, +3 oxidation state is most common i.e., Ln(III) compounds are predominant. However, +2 and +4 oxidation states can also be found in the solution or in solid compounds.

Q20 :

Compare the chemistry of actinoids with that of the lanthanoids with specialreference to:

(i) electronic configuration (iii) oxidation state

(ii) atomic and ionic sizes and (iv) chemical reactivity.

Answer :

(i) Electronic configuration

The general electronic configuration for lanthanoids is $[Xe]^{54}4f^{0-14}5d^{0-1}6s^2$and that for actinoids is $[Rn]^{86}5f^{0-14}6d^{0-1}7s^2$. Unlike 4*f*orbitals, 5*f* orbitals are not deeply buried and participate in bonding to a greater extent.

(ii) Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of + 2 and + 4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the 5*f*, 6*d*, and 7*s*levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

(iii) Atomic and Ionic sizes

Similar to lanthanoids, actinoids also exhibit actinoid contraction (overall decrease in atomic and ionic radii). The contraction is greater due to the poor shielding effect of 5*f*orbitals.

iv. **Chemical reactivity**

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

Q27 :

What are alloys? Name an important alloy which contains some of thelanthanoid 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.

Q28 :

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.

Answer :

Inner transition metals are those elements in which the last electron enters the *f*-orbital. The elements in which the 4*f* and the 5*f* 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.

Q29 :

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 primarily show three oxidation states (+2, +3, +4). Among these oxidation states, +3 state is the most common. Lanthanoids display a limited number of oxidation states because the energy difference between 4*f*, 5*d*, and 6*s*orbitals is quite large. On the other hand, the energy difference between 5*f*, 6*d*, and 7*s* orbitals is very less. Hence, actinoids display a large number of oxidation states. For example, uranium and plutonium display +3, +4, +5, and +6 oxidation states while neptunium displays +3, +4, +5, and +7. The most common oxidation state in case of actinoids is also +3.

Q33 :

Compare the chemistry of the actinoids with that of lanthanoids with reference to:

(i) electronic configuration

(ii) oxidation states and

(iii) chemical reactivity.

Answer :

Electronic configuration

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Oxidation states

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Chemical reactivity

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EXEMPLAR SOLUTIONS

13. Gadolinium belongs to 4*f* series. It's atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

(i) $[Xe]\ 4f^7 5d^1 6s^2$

(ii) $[Xe]\ 4f^6 5d^2 6s^2$

(iii) $[Xe]\ 4f^8 6d^2$

(iv) $[Xe]\ 4f^9 5s^1$

Ans : (i)

10. There are 14 elements in actinoid series. Which of the following elements does not belong to this series?

(i) U

(ii) Np

(iii) Tm

(iv) Fm

10. (iii)

41. Ionisation enthalpies of Ce, Pr and Nd are higher than Th, Pa and U. Why?

42. Although Zr belongs to 4*d* and Hf belongs to 5*d* transition series but it is quite difficult to separate them. Why?

43. Although +3 oxidation states is the characteristic oxidation state of lanthanoids but cerium shows +4 oxidation state also. Why?

41. **Hint :** It is because in the beginning, when 5*f* orbitals begin to be occupied, they will penetrate less into the inner core of electrons. The 5*f* electrons will therefore, be more effectively shielded from the nuclear charge than 4*f* electrons of the corresponding lanthanoids. Therefore outer electrons are less firmly held and they are available for bonding in the actinoids.

42. **Hint :** Due to lanthanoid contraction, they have almost same size (Zr, 160 pm) and (Hf, 159 pm).

43. It is because after losing one more electron Ce acquires stable $4f^0$ electronic configuration.

47. The second and third rows of transition elements resemble each other much more than they resemble the first row. Explain why?

47**. Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So they resemble each other much more as compared to first row elements.**

53. Match the compounds/elements given in Column I with uses given in Column II.

Column I (Compound/element)	Column II (Use)
(i) Lanthanoid oxide	(a) Production of iron alloy
(ii) Lanthanoid	(b) Television screen
(iii) Misch metal	(c) Petroleum cracking
(iv) Magnesium based alloy is constituent of	(d) Lanthanoid metal + iron
(v) Mixed oxides of lanthanoids are employed	(e) Bullets
	(f) In X-ray screen

53. (i) → (b) (ii) → (a) (iii) → (d) (iv) → (e) (v) → (c)

56. Match the solutions given in Column I and the colours given in Column II.

Column I (Aqueous solution of salt)	Column II (Colour)
(i) $FeSO_4.7H_2O$	(a) Green
(ii) $NiCl_2.4H_2O$	(b) Light pink
(iii) $MnCl_2.4H_2O$	(c) Blue
(iv) $CoCl_2.6H_2O$	(d) Pale green
(v) Cu_2Cl_2	(e) Pink
	(f) Colourless

56. (i) → (d) (ii) → (a) (iii) → (b) (iv) → (e) (v) → (f)

57. Match the property given in Column I with the element given in Column II.

Column I (Property)	Column II (Element)
(i) Lanthanoid which shows +4 oxidation state	(a) Pm
(ii) Lanthanoid which can show +2 oxidation state	(b) Ce
(iii) Radioactive lanthanoid	(c) Lu
(iv) Lanthanoid which has $4f^7$ electronic configuration in +3 oxidation state	(d) Eu
(v) Lanthanoid which has $4f^{14}$ electronic configuration in +3 oxidation state	(e) Gd
	(f) Dy

57. (i) → (b) (ii) → (d) (iii) → (a) (iv) → (e) (v) → (c)

60. Assertion : Separation of Zr and Hf is difficult.

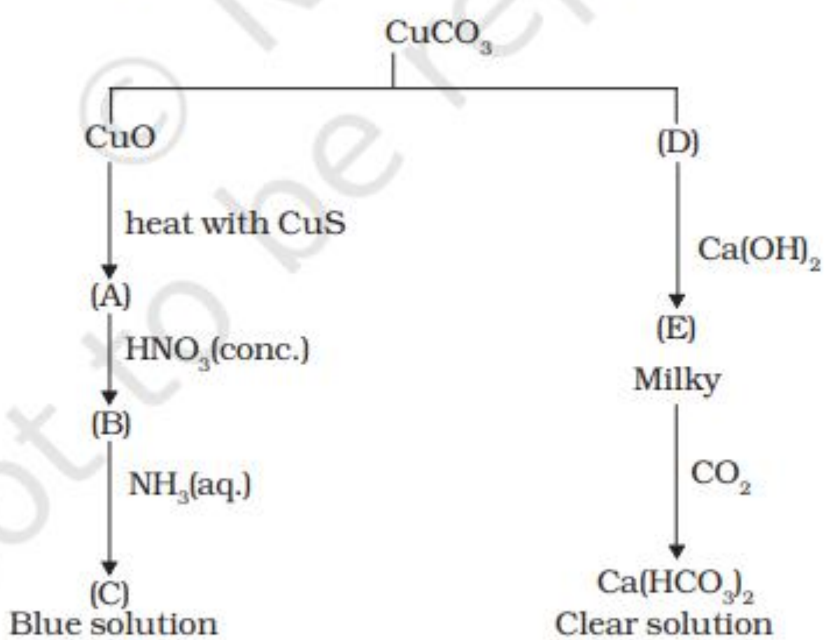
Reason : Because Zr and Hf lie in the same group of the periodic table.

61. Assertion : Actinoids form relatively less stable complexes as compared to lanthanoids.

Reason : Actinoids can utilise their 5*f* orbitals along with 6*d* orbitals in bonding but lanthanoids do not use their 4*f* orbital for bonding.

60. (ii) 61. (iii)

64. Identify A to E and also explain the reactions involved.



64. A = Cu   B = $Cu(NO_3)_2$ C = $[Cu(NH_3)_4]$ D = CO_2

E = $CaCO_3$ F = $Cu_2[Fe(CN)_6]$ G = $Ca(HCO_3)_2$

$$CuCO_3 \longrightarrow CuO + CO_2$$

$$CuO + CuS \longrightarrow \underset{(A)}{Cu} + SO_2$$

$$Cu + 4HNO_3\,(Conc) \longrightarrow \underset{(B)}{Cu(NO_3)_2} + 2NO + 2H_2O$$

$$\underset{(B)}{Cu^{2+}} + NH_3 \longrightarrow \underset{(C)}{[Cu(NH_3)_4]}$$

$$Ca(OH)_2 + \underset{(D)}{CO_2} \longrightarrow \underset{(E)}{CaCO_3} + H_2O$$

$$CaCO_3 + H_2O + CO_2 \longrightarrow Ca(HCO_3)_2$$

67. On the basis of Lanthanoid contraction, explain the following :

(i) Nature of bonding in La_2O_3 and Lu_2O_3.

(ii) Trends in the stability of oxo salts of lanthanoids from La to Lu.

(iii) Stability of the complexes of lanthanoids.

(iv) Radii of 4*d* and 5*d* block elements.

67. Hint : (i) As the size decreases covalent character increases. Therefore La2O3 is more ionic and Lu2O3 is more covalent.

(ii) As the size decreases from La to Lu, stability of oxo salts also decreases.

(iii) Stability of complexes increases as the size of lanthanoids decreases.

(iv) Radii of 4d and 5d block elements will be almost same.

(v) Acidic character of oxides increases from La to Lu.