Chapter 4: The d- and f-Block Elements

Exercises — Exercises

Q1 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

When transition metals form ions, ns electrons are lost before (n-1)d electrons. For lanthanoids and actinoids, outer s electrons are lost first, then f electrons.

(i) Cr (Z=24): [Ar] $3d_5\ 4s_1$
Cr^{3+} loses $4s_1$ and two 3d electrons: [Ar] $3d_3$

(ii) Pm (Z=61): [Xe] $4f_5\ 6s_2$
Pm^{3+} loses $6s_2$ and one 4f electron: [Xe] $4f_4$

(iii) Cu (Z=29): [Ar] $3d_{10}\ 4s_1$
Cu^{+} loses $4s_1$: [Ar] $3d_{10}$

(iv) Ce (Z=58): [Xe] $4f_1\ 5d_1\ 6s_2$
Ce^{4+} loses all 4 outer electrons: [Xe] (noble gas configuration)

(v) Co (Z=27): [Ar] $3d_7\ 4s_2$
Co^{2+} loses $4s_2$: [Ar] $3d_7$

(vi) Lu (Z=71): [Xe] $4f_{14}\ 5d_1\ 6s_2$
Lu^{2+} loses $6s_2$: [Xe] $4f_{14}\ 5d_1$

(vii) Mn (Z=25): [Ar] $3d_5\ 4s_2$
Mn^{2+} loses $4s_2$: [Ar] $3d_5$

(viii) Th (Z=90): [Rn] $6d_2\ 7s_2$
Th^{4+} loses $7s_2$ and $6d_2$: [Rn] (noble gas configuration)

Answer: (i) Cr^{3+}: [Ar] $3d_3$ (ii) Pm^{3+}: [Xe] $4f_4$ (iii) Cu^{+}: [Ar] $3d_{10}$ (iv) Ce^{4+}: [Xe] (v) Co^{2+}: [Ar] $3d_7$ (vi) Lu^{2+}: [Xe] $4f_{14}\ 5d_1$ (vii) Mn^{2+}: [Ar] $3d_5$ (viii) Th^{4+}: [Rn]

Q2 Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

SOLUTION

This question is about the relative stability of +3 vs +2 oxidation states for Mn and Fe.

Mn^{2+} has the configuration [Ar] $3d_5$ — a half-filled d subshell. This configuration is exceptionally stable because of:
- Maximum exchange energy (maximum number of parallel spins in degenerate orbitals)
- Symmetrical electron distribution

Oxidising Mn^{2+} to Mn^{3+} requires changing from $3d_5$ (half-filled, stable) to $3d_4$ (less stable). This requires a large amount of energy. The $E°(Mn^{3+}/Mn^{2+})$ = +1.57 V, indicating that Mn^{3+} is a powerful oxidant and Mn^{2+} strongly resists oxidation.

Fe^{2+} has the configuration [Ar] $3d_6$. Oxidation to Fe^{3+} gives $3d_5$ (half-filled), which is extra stable. Therefore Fe^{2+} is readily oxidised to Fe^{3+}, and $E°(Fe^{3+}/Fe^{2+})$ = +0.77 V confirms this.

In summary: Mn^{2+} -> Mn^{3+} destroys the stable half-filled d_5 configuration, making the process energetically very unfavourable. Fe^{2+} -> Fe^{3+} produces the stable d_5 configuration, making it energetically favourable.

Answer: Mn^{2+} ($3d_5$, half-filled) has exceptional extra stability due to maximum exchange energy. Oxidation to Mn^{3+} ($3d_4$) destroys this stability, so Mn^{2+} strongly resists oxidation. Fe^{2+} ($3d_6$) is readily oxidised to Fe^{3+} ($3d_5$, half-filled), which is extra stable. Hence Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to +3 state.

Q3 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

In the first half of the first row transition series (Sc to Mn), the +2 oxidation state becomes progressively more stable with increasing atomic number.

The +2 state is formed by removal of both 4s electrons, giving Mn^{+} ions with dn configurations. The stability of +2 state depends on the ease of removing the third electron (to reach +3).

As atomic number increases from Sc to Mn, the nuclear charge increases steadily. The d electrons added with increasing Z do not effectively shield the increasing nuclear charge from each other. This causes the d orbital energy to decrease gradually.

The third ionisation enthalpy (required to go from +2 to +3) generally increases across the series. Particularly notable: Mn^{2+} has the d_5 (half-filled) configuration with extra stability due to maximum exchange energy. Removing an electron from this stable configuration to form Mn^{3+} (d_4) requires very high energy.

Thus, as we go from Ti to Mn, the d subshell becomes progressively more stable, making it increasingly difficult to achieve the +3 state and stabilising the +2 state.

Answer: In the first half of the 3d series (Sc to Mn), increasing nuclear charge and the progressive filling of d orbitals raise the third ionisation enthalpy steadily. At Mn (d_5), the half-filled configuration has maximum exchange energy and exceptional stability. This makes removal of a further electron (to reach +3) increasingly difficult, so the +2 state becomes more and more stable across this range.

Q4 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

Electronic configurations play a major role — but not the only role — in determining the stability of oxidation states.

Key configurational factors:

1. Extra stability of d_0, d_5, and d_{10} configurations:
   - d_0: Sc^{3+} (no d electrons, noble-gas-like) — very stable
   - d_5: Mn^{2+} ($[Ar]_3d_5$, half-filled) — highly stable; Mn^{3+} readily oxidises back to Mn^{2+}
   - d_{10}: Zn^{2+} ($[Ar]_3d_{10}$, completely filled) — only oxidation state of Zn; Cu^{+} ($[Ar]_3d_{10}$) is stable in solids

2. Stability determined by E°(M^n+/M^(n-1)⁺) values:
   - $E°(Mn^{3+}/Mn^{2+})$ = +1.57 V: Mn^{3+} is strongly oxidising; Mn^{2+} very stable
   - $E°(Fe^{3+}/Fe^{2+})$ = +0.77 V: Fe^{3+} (d_5) is stable; Fe^{2+} is moderately reducing
   - $E°(Cr^{3+}/Cr^{2+})$ = -0.41 V: Cr^{3+} is very stable; Cr^{2+} is strongly reducing

3. Highest oxidation state limited by available d electrons:

- Ti can reach +4 (d_0 product), Mn can reach +7 (d_0 product in MnO_4^-)
- Beyond Mn, d electrons are too paired for high oxidation states to be reached by O or F alone

However, other factors also matter: hydration enthalpy, lattice energy, and the nature of ligands. Electronic configuration gives a good guide but is not the sole determinant.

Answer: Electronic configurations strongly influence oxidation state stability — particularly d_0, d_5, and d_{10} configurations confer extra stability (e.g., Mn^{2+}/d_5, Zn^{2+}/d_{10}, Cr^{3+}/d_3). However, hydration enthalpy, lattice energy, and ligand effects also play roles. The highest stable oxidation state coincides with the total number of s+d electrons up to Mn (group 7), after which higher states become unstable.

Q5 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

Ground state d-configurations of atoms include the 4s electrons. We need to identify the element and its stable ion.

$3d_3$: Element is V (Z=23) with [Ar] $3d_3\ 4s_2$

V can lose $4s_2$ to give V^{2+} ($3d_3$) or $4s_2$+one 3d to give V^{3+} ($3d_2$)

Most stable: V^{5+} (d_0, all electrons removed to group number) or V^{3+} (d_2); however for d_3 config in the atom, V^{2+} (stable $3d_3$) is common

Stable oxidation state from $3d_3$ atom: +5 (group number, VO_2^+) but also +2, +3

$3d_5$: Element is Mn (Z=25) with [Ar] $3d_5\ 4s_2$

Mn^{2+} = $3d_5$ (half-filled, very stable). Mn can also reach +7.

Most stable oxidation state with d_5 configuration in atom: +2 (gives d_5 ion with maximum stability)

$3d_8$: Element is Ni (Z=28) with [Ar] $3d_8\ 4s_2$

Ni^{2+} = $3d_8$ (loses $4s_2$). Ni rarely exceeds +2.

Most stable oxidation state: +2

$3d_4$: Taken as the element with the expected [Ar] $3d_4\ 4s_2$ filling, i.e. Cr (which actually adopts [Ar] $3d_5\ 4s_1$ in the ground state). The ions formed are Cr^{2+} ($3d_4$) or Cr^{3+} ($3d_3$).

Cr^{3+} (d_3) is the most stable state, since the d_3 configuration is a stable half-filled

t_2g level; Cr^{2+} (d_4) is a strong reducing agent.

Hence a d_4 atom shows +3 as its most stable oxidation state (giving the stable d_3 ion).

Answer: $3d_3$ (V): stable at +5 (d_0) and +3 (d_2), commonly +2 also; $3d_5$ (Mn): most stable at +2 (the d_5 ion has extra stability from half-filled subshell); $3d_8$ (Ni): most stable at +2 (d_8 loses $4s_2$); $3d_4$ (Cr, hypothetical): most stable at +3 (giving d_3 product).

Q6 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

We need oxometal anions where oxidation state of the metal = its group number in the periodic table.

Group 6 (Cr): CrO_4^{2-} (chromate ion) — Cr is in +6 oxidation state = group 6 number ✓
Also $Cr_2O_7^{2-}$ (dichromate ion) — Cr is in +6 oxidation state = group 6 number ✓

Group 7 (Mn): MnO_4^- (permanganate ion) — Mn is in +7 oxidation state = group 7 number ✓
Also MnO_4^{2-} (manganate ion) — Mn is in +6 oxidation state (not equal to group 7)

Group 5 (V): VO_4^{3-} (orthovanadate) and VO_3^- (metavanadate) — V is in +5 = group 5 ✓
Also VO_2^+ — V in +5 state

Other examples: TiO_4^{4-} (Ti in +4, group 4) and FeO_4^{2-} (Fe in +6, but Fe is in group 8, not equal)

Answer: The oxometal anions in which metal oxidation state equals group number: VO_4^{3-} and VO_2^+ (V = +5, group 5); CrO_4^{2-} and $Cr_2O_7^{2-}$ (Cr = +6, group 6); MnO_4^- (Mn = +7, group 7).

Q7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

SOLUTION

Definition of Lanthanoid Contraction:

The steady decrease in atomic and ionic radii of lanthanoid elements (La to Lu) with increasing atomic number is called lanthanoid contraction. As the 4f orbitals are progressively filled, each added electron does not effectively shield the next electron from the increasing nuclear charge because 4f electrons are poor at shielding each other. The result is a steady contraction in size from La (atomic radius ~187 pm) to Lu (~174 pm).

Consequences of Lanthanoid Contraction:

1. Similarity in properties of 2nd and 3rd row transition elements:

The size increase expected from the 4d to 5d series is almost exactly compensated by lanthanoid contraction. As a result, corresponding members of the 4d and 5d transition series have nearly identical atomic radii.

Example: Zr (160 pm) ≈ Hf (159 pm); Mo ≈ W; Nb ≈ Ta

These pairs have very similar physical and chemical properties, making their separation from each other very difficult (e.g., Zr and Hf always occur together in nature).

2. Difficulty in separation of lanthanoids from each other:

The gradual decrease in size leads to very similar properties among the lanthanoids themselves. Their separation from each other requires special techniques like ion-exchange chromatography.

3. Basicity differences:

As ionic radius decreases from La^{3+} to Lu^{3+}, the hydroxides become less basic. $La(OH)_3$ is more basic than $Lu(OH)_3$.

Answer: Lanthanoid contraction is the steady decrease in atomic and ionic radii of the lanthanoid elements (La to Lu) due to the ineffective shielding of 4f electrons. Consequences: (1) 4d and 5d transition metals in the same group have nearly identical radii and properties (e.g., Zr ≈ Hf), making their separation difficult; (2) lanthanoids themselves have very similar properties, making their mutual separation hard; (3) basicity of lanthanoid hydroxides decreases from La to Lu.

Q8 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

Why called transition elements:

According to IUPAC, transition metals are defined as metals which have an incomplete d subshell either in the neutral atom or in their common ions. They were originally called 'transition' because their properties were transitional between those of the s- and p-block elements.

Characteristics of transition elements:

1. Variable oxidation states — due to incomplete d subshell and comparable energies of (n-1)d and ns orbitals
2. Formation of coloured ions — d-d electronic transitions absorb visible light
3. Paramagnetic behaviour — presence of unpaired d electrons
4. Catalytic properties — ability to change oxidation states and form complexes
5. Complex compound formation — small ionic size, high charge, and available d orbitals for bonding
6. Formation of interstitial compounds — small atoms (H, C, N) can be trapped in d-metal crystal lattices
7. Alloy formation — similar atomic radii (within ~15%) allows mixing
8. High melting and boiling points — strong metallic bonding due to involvement of d electrons
9. High enthalpies of atomisation — many unpaired electrons in atoms lead to strong interatomic interactions

d-Block elements NOT regarded as transition elements:

Zinc (Zn, Z=30), cadmium (Cd, Z=48), and mercury (Hg, Z=80) have completely filled d_{10} configuration in both their ground state and in their common oxidation state (+2, giving d_{10}). Since d orbitals are always completely filled, they do not satisfy the IUPAC definition and are not transition metals (though their chemistry is discussed alongside transition metals as they are end members of their respective series).

Answer: Transition elements are d-block elements with incomplete d subshell in neutral atom or common ions. Characteristics: variable oxidation states, coloured ions, paramagnetism, catalytic activity, complex formation, interstitial compound formation, high mp/bp. Zn, Cd, and Hg are not regarded as transition elements because they have completely filled d_{10} configuration in both atom and common (+2) ions.

Q9 In what way is the electronic configuration of the transition elements different from that of the non transition elements?

SOLUTION

Non-transition (main group) elements:
Their outermost electrons occupy s or p orbitals of the outermost shell. The general configuration is ns_1-2 or ns_2 np_1-6. There are no partially filled inner d or f orbitals in the commonly occurring forms.

Transition elements (d-block):
Their outermost electrons (ns_1-2) are in the outermost shell, but they also have partially filled (n-1)d orbitals in the penultimate shell. The general configuration is (n-1)d_1-10 ns_1-2.

Key differences:
1. Transition elements have electrons in two outer shells simultaneously — the ns shell and the (n-1)d inner shell — both of which can participate in bonding and reactions.
2. The (n-1)d orbital energy is close to that of ns, allowing variable number of electrons to be involved in bonding.
3. This leads to variable oxidation states, which is characteristic of transition metals but absent in most non-transition elements.
4. Non-transition elements show fixed or limited oxidation states (differing by 2 units, as in inert pair effect for p-block), while transition elements exhibit oxidation states differing by 1 unit.

Example: Fe has [Ar] $3d_6$ $4s_2$ — both 3d and 4s electrons are available for bonding. In contrast, Ca has [Ar] $4s_2$ — only 4s electrons are available.

Answer: Transition elements have partially filled (n-1)d orbitals in addition to the outermost ns electrons, giving configuration (n-1)d_{1-10} ns_{1-2}. Non-transition elements have only s or p electrons in their outermost shells (ns_{1-2} or ns_2 np_{1-6}), with no partially filled inner d orbitals. The involvement of both ns and (n-1)d electrons in transition metals leads to variable oxidation states differing by 1 unit, whereas non-transition elements show fixed oxidation states or states differing by 2 units.

Q10 What are the different oxidation states exhibited by the lanthanoids?

SOLUTION

The lanthanoids (cerium to lutetium, Z = 58 to 71) primarily exhibit the +3 oxidation state in their compounds.

Principal oxidation state: +3
All lanthanoids form stable Ln^{3+} ions. This is the most common and most stable oxidation state for all 14 lanthanoids. The tripositive state arises from loss of two 6s electrons and one 4f electron.

Occasional +4 oxidation state:
- Ce^{4+}: Cerium (Z=58) can lose one 4f electron to give Ce^{4+} with the stable [Xe] noble gas configuration. However, Ce^{4+} is a strong oxidant.
- Tb^{4+} and Pr^{4+}, Nd^{4+} also exhibit +4 state, mainly in solid oxides (MO_2). Tb^{4+} corresponds to a half-filled $4f^7$ configuration.

Occasional +2 oxidation state:
- Eu^{2+} (Z=63): Eu has $[Xe]_4f^7$ $6s_2$; loss of only 2 outer electrons gives Eu^{2+} with the stable half-filled $4f^7$ configuration.
- Yb^{2+} (Z=70): Yb has $[Xe]_4f^{14}$ $6s_2$; Yb^{2+} has the completely filled $4f^{14}$ configuration.
- Sm^{2+} and Tm^{2+} also show +2 state occasionally.

The occurrence of +2 and +4 states arises from the extra stability of empty (f^0), half-filled (f^7), or completely filled (f^{14}) f subshells.

Answer: Lanthanoids predominantly exhibit the +3 oxidation state. Occasionally, +4 is shown by Ce (forming stable [Xe] configuration), Tb (forming f^7 half-filled), and Pr, Nd, Dy in oxides. The +2 state is shown by Eu (forming stable f^7) and Yb (forming stable f^{14}). These deviations from +3 arise from extra stability of f^0, f^7, and f^{14} configurations.

Q11 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) Paramagnetic behaviour:

Paramagnetism arises from the presence of unpaired electrons. Transition metals have partially filled d orbitals which contain one or more unpaired electrons (following Hund's rule). Each unpaired electron has a spin magnetic moment of 1.73 BM. The observed magnetic moment is given by the spin-only formula: mu = sqrt[n(n+2)] BM, where n = number of unpaired electrons. Since most transition metal ions (e.g., Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}) have 1-5 unpaired d electrons, they are paramagnetic. Only d_0 (Sc^{3+}, Ti^{4+}) and d_{10} (Zn^{2+}, Cu^{+}) ions are diamagnetic.

(ii) High enthalpies of atomisation:

Transition metals have high enthalpies of atomisation because metallic bonding in these metals involves not only the ns electrons but also the (n-1)d electrons. With more unpaired electrons available for metallic bond formation, there are stronger interatomic interactions. The maxima in enthalpies of atomisation occur near the middle of each series (where the number of unpaired d electrons is maximum: d_5 configuration), indicating that one unpaired electron per d orbital is particularly favourable for strong interatomic interaction.

(iii) Formation of coloured compounds:

Transition metal ions in compounds have partially filled d orbitals. When visible light falls on these compounds, electrons undergo d-d transitions — an electron is excited from a lower energy d orbital to a higher energy d orbital. The energy absorbed corresponds to a particular wavelength (frequency) of visible light. The observed colour is the complementary colour of the light absorbed. The frequency absorbed depends on the nature of the metal ion and the ligands. Compounds of d_0 (Sc^{3+}, Ti^{4+}) and d_{10} (Zn^{2+}, Cu^{+}) ions are generally colourless because no d-d transitions are possible.

(iv) Catalytic properties:

Transition metals are good catalysts due to two main reasons:

- Ability to exhibit variable oxidation states: They can act as both electron donors and acceptors in intermediate steps (e.g., Fe^{3+}/Fe^{2+} in the persulphate-iodide reaction), providing alternative reaction pathways with lower activation energies.

- Ability to form complexes and adsorb reactants: Transition metals can adsorb reactant molecules on their surface through formation of weak bonds using d orbitals, increasing the local concentration and weakening bonds in reactant molecules. This lowers activation energy and increases reaction rate.

Answer: (i) Transition metals/ions have unpaired d electrons that produce spin magnetic moments, causing paramagnetism. (ii) High enthalpies of atomisation arise from involvement of (n-1)d electrons in metallic bonding in addition to ns electrons, giving stronger interatomic interactions. (iii) Coloured compounds result from d-d electronic transitions in partially filled d orbitals that absorb specific wavelengths of visible light. (iv) Catalytic activity arises from variable oxidation states (allowing intermediate electron transfer) and ability to adsorb and activate reactants on metal surfaces.

Q12 What are interstitial compounds? Why are such compounds well known for transition metals?

SOLUTION

Interstitial compounds are compounds formed when small atoms such as hydrogen (H), carbon (C), or nitrogen (N) are trapped inside the crystal lattices of transition metals (in the voids or interstices between metal atoms).

Examples: TiC, Mn_4N, Fe_3H, $VH_{0.56}$, $TiH_{1.7}$, etc.

These compounds are usually non-stoichiometric (no fixed atom ratio). They are neither purely ionic nor purely covalent. The small atoms occupy the interstitial voids in the close-packed metal structure.

Properties of interstitial compounds:
1. Very high melting points — higher than those of the pure metals
2. Extremely hard — some borides approach diamond in hardness
3. Retain metallic conductivity — still good conductors of electricity
4. Chemically inert

Why are they well known for transition metals?
Transition metals are well known for forming interstitial compounds because:
1. Transition metals have larger atomic radii (especially 4d and 5d series) that provide spacious lattice interstices suitable for accommodating small atoms like H, C, and N.
2. The partially filled d orbitals of transition metals can form bonds (through d

orbital overlap) with these small atoms, providing some degree of stabilisation.
3. The metallic bonding in transition metals is strong and the crystal structure (bcc, hcp, ccp) provides sufficient tetrahedral and octahedral voids for small atoms to occupy.

Answer: Interstitial compounds form when small atoms (H, C, N) are trapped in the crystal lattice voids of transition metals (e.g., TiC, Mn_4N, Fe_3H). They are non-stoichiometric, hard, have high melting points, retain metallic conductivity, and are chemically inert. They are well known for transition metals because these metals have large atomic radii with spacious lattice interstices and partially filled d orbitals capable of bonding with the small interstitial atoms.

Q13 How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples.

SOLUTION

Transition metals — variability in oxidation states:
Transition metals show multiple oxidation states that differ from each other by one unit. This is because both the (n-1)d electrons and the ns electrons are available for bonding, and the energy gap between adjacent d orbital-based states is small.
Example: Vanadium (V) shows +2, +3, +4, +5; chromium shows +2, +3, +4, +5, +6; manganese shows +2, +3, +4, +5, +6, +7.
The variability spans a wide range, e.g., Mn goes from +2 to +7.

Non-transition metals — variability in oxidation states:
Non-transition elements in the p-block show oxidation states that typically differ by 2 units. This is because only the outer ns_2 pair can be inert (inert pair effect) or both electrons of a pair can be released together. The variation follows group valency and group valency minus 2.
Examples:
- Sn: +2 and +4 (differ by 2)
- Pb: +2 and +4 (differ by 2; +2 more stable due to inert pair effect)
- Cl: -1, +1, +3, +5, +7 (these differ by 2)
- S: -2, 0, +2, +4, +6 (differ by 2)

Key contrast:
Transition metals: oxidation states differ by 1 unit (due to sequential d electron removal)
Non-transition metals: oxidation states differ by 2 units (due to inert pair effect and

electron pair involvement)

Answer: In transition metals, oxidation states differ by 1 unit (e.g., V: +2, +3, +4, +5; Mn: +2 to +7) because both ns and (n-1)d electrons are available sequentially. In non-transition (p-block) metals, oxidation states differ by 2 units (e.g., Sn: +2 and +4; Pb: +2 and +4) due to the inert pair effect and removal of electron pairs. The range of oxidation states in transition metals is far wider than in non-transition metals.

Q14 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 from Iron Chromite Ore ($FeCr_2O_4$):

Step 1 — Alkaline fusion with Na_2CO_3 in air:
The chromite ore is fused with sodium carbonate (Na_2CO_3) in free access of air at high temperature. Chromium is oxidised from +3 to +6, forming sodium chromate (Na_2CrO_4 — yellow solution):
$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$

Step 2 — Acidification to form sodium dichromate:
The yellow solution of Na_2CrO_4 is filtered and acidified with H_2SO_4 (or by passing CO_2). The chromate ions are converted to dichromate ions (orange colour):
$2\ Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
Or in ionic form: $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
$Na_2Cr_2O_7.2H_2O$ crystallises out.

Step 3 — Conversion to potassium dichromate:
Sodium dichromate (more soluble) is treated with potassium chloride solution. Potassium dichromate (less soluble) crystallises out:
$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$

Effect of increasing pH on potassium dichromate solution:
Chromate (CrO_4^{2-}, yellow) and dichromate ($Cr_2O_7^{2-}$, orange) are interconvertible in aqueous solution depending on pH:
$2\ CrO_4^{2-} + 2\ H^+ \Leftrightarrow Cr_2O_7^{2-} + H_2O$

In acidic medium (low pH): equilibrium shifts right — dichromate (orange) is the predominant species.
On increasing pH (adding alkali): equilibrium shifts left — dichromate is converted

to chromate (yellow).

$Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2\ CrO_4^{2-} + H_2O$

Thus, increasing pH converts the orange dichromate solution to a yellow chromate solution. The oxidation state of Cr (+6) remains the same in both forms.

Answer: $K_2Cr_2O_7$ preparation: (1) Fuse $FeCr_2O_4$ with Na_2CO_3 + air → Na_2CrO_4 ($4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$); (2) acidify to give $Na_2Cr_2O_7$ ($2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$); (3) treat with KCl → $K_2Cr_2O_7$ (less soluble) crystallises. Increasing pH converts orange dichromate to yellow chromate: $Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$.

Q15 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 a strong oxidising agent. In acidic solution, the dichromate ion accepts electrons and is reduced from Cr(+6) to Cr^{3+}:

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow 2\ Cr^{3+} + 7\ H_2O$ ($E^\circ = +1.33$ V)

(i) Reaction with iodide (I^-):

Iodide is oxidised to iodine (I_2). Half-reaction for oxidation of I^-:

$6\ I^- \rightarrow 3\ I_2 + 6\ e^-$

Combined ionic equation:

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

Verification: Cr: 2=2 ✓; I: 6=6 ✓; O: 7=7 ✓; H: 14=14 ✓; Charge: LHS = -2+14-6 = +6; RHS = +6+0 = +6 ✓

(ii) Reaction with iron(II) solution (Fe^{2+}):

Fe^{2+} is oxidised to Fe^{3+}. Half-reaction:

$6\ Fe^{2+} \rightarrow 6\ Fe^{3+} + 6\ e^-$

Combined ionic equation:

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

Verification: Charge: LHS = -2+14+12 = +24; RHS = +6+18 = +24 ✓

(iii) Reaction with H_2S:

H_2S is oxidised to elemental sulphur (S). Each H_2S loses 2 electrons; $3H_2S$ provides 6 electrons:

$3\ H_2S \rightarrow 3\ S + 6\ H^+ + 6\ e^-$

Combined ionic equation:

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

Verification: H: 8+6=14=14 ✓; S: 3=3 ✓; O: 7=7 ✓; Charge: LHS = -2+8 = +6; RHS = +6 ✓

Answer: Dichromate in acid: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$. Reactions: (i) with I^-: $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$; (ii) with Fe^{2+}: $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$; (iii) with H_2S: $Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$.

Q16 Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid? Write the ionic equations for the reactions.

SOLUTION

Preparation of Potassium Permanganate ($KMnO_4$):

Step 1 — Alkaline fusion of MnO_2:
Pyrolusite ore (MnO_2) is fused with KOH (or NaOH) in the presence of an oxidising agent (KNO_3 or air). This produces the dark green potassium manganate (K_2MnO_4):
$2\ MnO_2 + 4\ KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2\ H_2O$

Step 2 — Disproportionation of manganate to permanganate:
In neutral or acidic solution, the green K_2MnO_4 disproportionates to give $KMnO_4$ (purple) and MnO_2:
$3\ MnO_4^{2-} + 4\ H^+ \rightarrow 2\ MnO_4^- + MnO_2 + 2\ H_2O$

Commercially, the K_2MnO_4 is oxidised electrolytically in alkaline solution:
$MnO_4^{2-} \rightarrow MnO_4^- + e^-$ (at anode)

Oxidising reactions of acidified $KMnO_4$ ($MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$, E° = +1.52 V):

(i) Reaction with Fe^{2+} ions:
Fe^{2+} is oxidised to Fe^{3+}. Half-reaction: $5\ Fe^{2+} \rightarrow 5\ Fe^{3+} + 5\ e^-$
Ionic equation: $MnO_4^- + 8\ H^+ + 5\ Fe^{2+} \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4\ H_2O$
Verification: Charge LHS = -1+8+10 = +17; RHS = +2+15 = +17 ✓

(ii) Reaction with SO_2:
SO_2 is oxidised to SO_4^{2-} (each S goes from +4 to +6, losing 2 electrons).
Half-reaction: $5\ SO_2 + 10\ H_2O \rightarrow 5\ SO_4^{2-} + 20\ H^+ + 10\ e^-$

Combining with 2 MnO_4^- (gaining 10 e^-) and cancelling H^+/H_2O:
5 SO_2 + 2 MnO_4^- + 2 H_2O -> 5 SO_4^{2-} + 2 Mn^{2+} + 4 H^+
Verification: S: 5=5; Mn: 2=2; O: LHS = 10+8+2 = 20, RHS = 20 ✓; H: LHS = 4, RHS = 4 ✓; Charge: LHS = -2, RHS = -10+4+4 = -2 ✓

(iii) Reaction with oxalic acid ($H_2C_2O_4$ or $C_2O_4^{2-}$):
Oxalate is oxidised to CO_2 (C goes from +3 to +4, each $C_2O_4^{2-}$ loses 2 electrons).
Half-reaction: 5 $C_2O_4^{2-}$ -> 10 CO_2 + 10 e^-
Combined ionic equation:
2 MnO_4^- + 16 H^+ + 5 $C_2O_4^{2-}$ -> 2 Mn^{2+} + 8 H_2O + 10 CO_2
Verification: Charge LHS = -2+16-10 = +4; RHS = +4 ✓; C: 10=10 ✓; O: 8+20=28=16+8 ✓

Answer: $KMnO_4$ prepared by: (1) fusing MnO_2 + KOH + O_2 -> K_2MnO_4; (2) disproportionation in acid: 3MnO_4^{2-} + 4H^+ -> 2MnO_4^- + MnO_2 + 2H_2O; or electrolytic oxidation of K_2MnO_4. Acidified $KMnO_4$ reactions: (i) with Fe^{2+}: MnO_4^- + 8H^+ + 5Fe^{2+} -> Mn^{2+} + 5Fe^{3+} + 4H_2O; (ii) with SO_2: 5SO_2 + 2MnO_4^- + 2H_2O -> 5SO_4^{2-} + 2Mn^{2+} + 4H^+; (iii) with oxalic acid: 2MnO_4^- + 16H^+ + 5$C_2O_4^{2-}$ -> 2Mn^{2+} + 8H_2O + 10CO_2.

Q17 For M^{2+}/M and M^{3+}/M^{2+} systems the E° 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

(i) Stability of Fe^{3+} compared to Cr^{3+} and Mn^{3+} in acid solution:

The E°(M^{3+}/M^{2+}) value indicates the tendency of M^{3+} to be reduced to M^{2+}:
- E°(Cr^{3+}/Cr^{2+}) = -0.4 V: Very negative — Cr^{3+} is very reluctant to be reduced to Cr^{2+}. Cr^{3+} is extremely stable; it is a poor oxidising agent. Cr^{2+} is a strong reducing agent.
- E°(Fe^{3+}/Fe^{2+}) = +0.8 V: Moderately positive — Fe^{3+} can oxidise moderate reducing agents but is not a powerful oxidant. Fe^{3+} has moderate stability in acid solution.
- E°(Mn^{3+}/Mn^{2+}) = +1.5 V: Large positive value — Mn^{3+} is a very powerful oxidising agent and is highly unstable in acid solution (it oxidises water and reduces to Mn^{2+}).

Order of stability of +3 state in acid: Cr^{3+} >> Fe^{3+} >> Mn^{3+}
Cr^{3+} is the most stable (d_3, half-filled t_2g); Mn^{3+} is the least stable (d_4, drives to the more stable d_5 of Mn^{2+}).

(ii) Ease of oxidation of metal to M^{2+}:

$E°(M^{2+}/M)$ values indicate how readily the metal is oxidised. More negative E° = easier oxidation:
- $E°(Mn^{2+}/Mn)$ = -1.2 V: Most negative — Mn is oxidised most easily
- $E°(Cr^{2+}/Cr)$ = -0.9 V: Very negative — Cr is also easily oxidised
- $E°(Fe^{2+}/Fe)$ = -0.4 V: Less negative — Fe is harder to oxidise

Order of ease of oxidation: Mn > Cr > Fe
Fe is the most difficult to oxidise among the three metals. Both Mn and Cr are more easily oxidised than Fe.

Answer: (i) Stability of +3 state in acid: Cr^{3+} (E° for Cr^{3+}/Cr^{2+} = -0.4V) is the most stable — it resists reduction strongly. Fe^{3+} (E° = +0.8V) is moderately stable. Mn^{3+} (E° = +1.5V) is the least stable — a powerful oxidant that rapidly converts to Mn^{2+} (d_5). Order: Cr^{3+} >> Fe^{3+} >> Mn^{3+}. (ii) Ease of oxidation of metals: $E°(Mn^{2+}/Mn)$ = -1.2V, $E°(Cr^{2+}/Cr)$ = -0.9V, $E°(Fe^{2+}/Fe)$ = -0.4V. Order of ease of oxidation: Mn > Cr > Fe. Iron is the hardest to oxidise of the three.

Q18 Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^{2+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

SOLUTION

Colour in transition metal ions arises from d-d electronic transitions. An ion is coloured only if it has at least one electron and at least one vacancy in d orbitals (i.e., partially filled d orbitals, not d_0 or d_{10}).

Ti^{3+} (Z=22): Configuration is [Ar] $3d_1$. Has 1 unpaired d electron; d-d transition is possible. COLOURED (purple/violet in aqueous solution).

V^{3+} (Z=23): Configuration is [Ar] $3d_2$. Has 2 d electrons; d-d transition possible. COLOURED (green).

Cu^{2+} (Z=29): Configuration is [Ar] $3d_9$. Has 9 d electrons (1 vacancy); d-d transition possible. COLOURED (blue in aqueous solution).

Sc^{3+} (Z=21): Configuration is [Ar] $3d_0$ (d_0). No d electrons — no d-d transition possible. COLOURLESS.

Mn^{2+} (Z=25): Configuration is [Ar] $3d_5$ (half-filled). All 5 d orbitals have 1 electron each. In principle, d-d transitions require a spin flip (they are spin-forbidden) because all electrons have parallel spins in the half-filled configuration. Spin-forbidden transitions give only a very faint colour. Mn^{2+} is very FAINTLY PINK (almost colourless) in aqueous solution.

Fe^{3+} (Z=26): Configuration is [Ar] $3d_5$. Same as Mn^{2+}. Spin-forbidden d-d transitions only. Fe^{3+} is very FAINTLY YELLOW in dilute aqueous solution (due to hydrolysis; the colour is mostly due to $[Fe(H_2O)_5(OH)]^{2+}$ formation, not pure d-d transition).

Co^{2+} (Z=27): Configuration is [Ar] $3d_7$. Has 3 unpaired electrons; d-d transitions readily possible. COLOURED (pink in aqueous solution).

Summary: Ti^{3+}, V^{3+}, Cu^{2+}, Mn^{2+}, Fe^{3+}, and Co^{2+} are coloured (Mn^{2+} and Fe^{3+} very faintly); Sc^{3+} is colourless.

Answer: Coloured: Ti^{3+} (d_1, purple), V^{3+} (d_2, green), Cu^{2+} (d_9, blue), Co^{2+} (d_7, pink) — all have partially filled d orbitals allowing d-d transitions. Mn^{2+} (d_5) and Fe^{3+} (d_5): only faint colour as d-d transitions are spin-forbidden (all 5 d electrons with parallel spins). Colourless: Sc^{3+} (d_0) — no d electrons, no d-d transitions possible.

Q19 Compare the stability of +2 oxidation state for the elements of the first transition series.

SOLUTION

The stability of +2 state across the first transition series (Sc to Zn) varies considerably:

Sc (Z=21): Sc^{2+} would be $[Ar]_3d_1$. Sc strongly prefers +3 (d_0, noble gas config). Sc^{2+} is virtually unknown.

Ti (Z=22): Ti^{2+} = $[Ar]_3d_2$. Ti prefers +4 and +3. Ti^{2+} exists but is unstable, a strong reducing agent.

V (Z=23): V^{2+} = $[Ar]_3d_3$. Stable aquo ion; V^{2+} is a strong reducing agent. Less stable than Mn^{2+}.

Cr (Z=24): Cr^{2+} = $[Ar]_3d_4$. Moderately stable but is a strong reducing agent ($E°(Cr^{2+}/Cr)$ = -0.9V); readily oxidised to Cr^{3+}.

Mn (Z=25): Mn^{2+} = $[Ar]_3d_5$ (half-filled subshell). Most stable +2 state in the first half due to extra stability of half-filled d_5 configuration. $E°(Mn^{3+}/Mn^{2+})$ = +1.57 V shows

very high resistance to oxidation to +3.

Fe (Z=26): Fe^{2+} = $[Ar]_3d_6$. Stable in aqueous solution but can be oxidised to Fe^{3+} (d_5) — this conversion is facile because Fe^{3+} (d_5) gains extra stability ($E°(Fe^{3+}/Fe^{2+})$ = +0.77V).

Co (Z=27): Co^{2+} = $[Ar]_3d_7$. Stable in aqueous solution; Co^{3+} is strongly oxidising in the absence of complexing ligands.

Ni (Z=28): Ni^{2+} = $[Ar]_3d_8$. Very stable; Ni rarely exhibits +3 or higher state. The highest negative hydration enthalpy helps stabilise Ni^{2+}.

Cu (Z=29): Cu^{2+} = $[Ar]_3d_9$. Stable in aqueous solution due to large hydration enthalpy. Cu^{+} (d_{10}) tends to disproportionate in water.

Zn (Z=30): Zn^{2+} = $[Ar]_3d_{10}$ (filled d). The only common oxidation state of Zn; very stable. Zn^{2+} has no d-d transition (colourless); only +2 state known.

Overall stability order of +2 state:
Least stable: $Sc^{2+} < Ti^{2+} < V^{2+} < Cr^{2+} << Mn^{2+} > Fe^{2+} > Co^{2+} < Ni^{2+} > Cu^{2+} >> Zn^{2+}$
Mn^{2+} is particularly stable due to half-filled d_5; Zn^{2+} is stable due to d_{10}; Ni^{2+} is notably stable due to high hydration enthalpy.

Answer: Sc^{2+}: virtually unknown (prefers d_0 in +3); Ti^{2+}, V^{2+}, Cr^{2+}: unstable, strong reducing agents. Mn^{2+} (d_5): most stable in first half — extra stability from half-filled d subshell. Fe^{2+}: stable but readily oxidised to Fe^{3+} (d_5). Co^{2+}: stable, Co^{3+} strongly oxidising without ligands. Ni^{2+}: very stable (high negative hydration enthalpy). Cu^{2+}: stable in water. Zn^{2+} (d_{10}): most stable, only oxidation state. Stability peaks at Mn (d_5) and Zn (d_{10}) due to extra configurational stability.

Q20 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: General configuration [Xe] $4f_{1-14}$ $5d_{0-1}$ $6s_2$. The 4f orbitals are filled progressively. The 4f orbitals are inner orbitals, well shielded and buried inside the atom — 4f electrons participate very little in bonding.
Actinoids: General configuration [Rn] $5f_{1-14}$ $6d_{0-2}$ $7s_2$. The 5f orbitals are filled progressively. Unlike 4f, the 5f orbitals are not as deeply buried — they extend

further outward and are better exposed to the external environment, so 5f electrons can participate in bonding to a far greater extent. There are many more exceptions and irregularities in the configurations of actinoids.

(ii) Atomic and Ionic Sizes:
Both series show a gradual contraction with increasing atomic number — lanthanoid contraction and actinoid contraction respectively.
The actinoid contraction is greater from element to element than lanthanoid contraction because 5f electrons provide even poorer shielding than 4f electrons.
Overall, actinoids are larger than the corresponding lanthanoids.

(iii) Oxidation States:
Lanthanoids: Predominantly +3; +2 (Eu, Yb, Sm) and +4 (Ce, Tb) shown rarely, stabilised by f_0, f_7, or f_{14} configurations. Range of oxidation states is narrow: +2, +3, +4.
Actinoids: Show a much wider range of oxidation states, especially in the early members. For example: Pa (+3 to +5), U (+3 to +6), Np (+3 to +7), Pu (+3 to +7). This is because 5f, 6d, and 7s levels are of comparable energies, so more electrons are available for bonding. The later actinoids (from Cm onwards) show predominantly +3, becoming more like lanthanoids.

(iv) Chemical Reactivity:
Lanthanoids: Early members are quite reactive (like Ca), later ones behave more like Al. They react with water, dilute acids, and halogens. They form Ln_2O_3 and $Ln(OH)_3$. They are not very reactive at room temperature but react on heating.
Actinoids: Highly reactive metals, especially when finely divided. React with boiling water (giving oxide/hydride mixture), most non-metals at moderate temperatures, and HCl attacks all of them. Many are resistant to HNO_3 due to protective oxide layers. Most are strongly radioactive, complicating their study.

Answer: (i) Electronic config: lanthanoids fill 4f (buried, non-bonding); actinoids fill 5f (more exposed, can bond). (ii) Sizes: both show contraction along series; actinoid contraction is larger than lanthanoid contraction per element. (iii) Oxidation states: lanthanoids mainly +3 (some +2, +4); actinoids show wide range (+3 to +7 for early members) because 5f, 6d, 7s levels are comparable in energy. (iv) Reactivity: lanthanoids moderately reactive; actinoids highly reactive and mostly radioactive, forming protective oxide films with HNO_3.

Q21 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^{2+} (d_4) is strongly reducing while Mn^{3+} (d_4) is strongly oxidising:
Both have d_4 configuration but their behaviour is opposite.
Cr^{2+} (d_4): To become more stable, Cr^{2+} tends to lose one electron and become Cr^{3+} (d_3). The d_3 configuration corresponds to a half-filled t_2g level in an octahedral field — this is exceptionally stable. So Cr^{2+} is a strong reducing agent because the d_4 -> d_3 transition is energetically very favourable.
Mn^{3+} (d_4): Mn^{3+} tends to gain one electron and become Mn^{2+} (d_5, half-filled). The d_5 configuration has extra stability (maximum exchange energy). So Mn^{3+} readily accepts electrons (is a strong oxidant) to achieve the stable d_5 configuration.
$E°(Cr^{3+}/Cr^{2+})$ = -0.41V (Cr^{2+} is reducing); $E°(Mn^{3+}/Mn^{2+})$ = +1.57V (Mn^{3+} is oxidising).

(ii) Cobalt(II) stable in water but easily oxidised in presence of complexing agents:
In aqueous solution, Co^{2+} (d_7) is kinetically stable. The $E°(Co^{3+}/Co^{2+})$ = +1.97V in aqueous solution, which means Co^{3+} (aq) is a very strong oxidant and would oxidise water. So Co^{3+} (aq) is essentially unstable and the reverse (Co^{3+} -> Co^{2+}) is favoured.
However, when complexing ligands are present (e.g., NH_3, CN^-), they form stable Co^{3+} complexes by lowering the energy of the d_6 Co^{3+} state through crystal field stabilisation energy (CFSE). Co^{3+} in octahedral fields of strong ligands has d_6 low-spin configuration (t_2g^6) with very high CFSE. The $E°(Co^{3+}/Co^{2+})$ in the presence of NH_3 drops from +1.97V to about -0.83V. So Co(II) is readily oxidised to Co(III) in presence of complexing ligands.

(iii) d_1 configuration is very unstable in ions:
A d_1 ion (e.g., Ti^{3+}, V^{4+}) has only one d electron. This single electron has strong tendency to either be lost (giving d_0, noble-gas-like stable configuration) or pair up. Ions with d_1 configuration are strong reducing agents because removing one more electron achieves the very stable d_0 configuration. For example, Ti^{3+} (d_1) readily reduces to Ti^{4+} (d_0) or Ti^{2+} disproportionates. V^{5+} (d_0) and Ti^{4+} (d_0) are much more stable. The d_1 state is thus transient and highly reactive.

Answer: (i) Cr^{2+} (d_4) is reducing because $d_4 \rightarrow d_3$ (half-filled t_{2g}) is highly favourable; Mn^{3+} (d_4) is oxidising because $d_4 \rightarrow d_5$ (half-filled, maximum exchange energy) is highly favourable. (ii) Co^{2+} is stable in water but E° drops greatly in presence of complexing ligands (strong-field ligands stabilise Co^{3+} via CFSE), making Co(III) complexes thermodynamically stable. (iii) d_1 ions are unstable because losing the single d electron achieves the extra-stable d_0 (noble-gas-like) configuration; d_1 is always a strong reducing agent.

Q22 What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

SOLUTION

Definition:

Disproportionation is the process in which an element in a single oxidation state is simultaneously oxidised (to a higher oxidation state) and reduced (to a lower oxidation state) in the same reaction. In other words, when a particular oxidation state becomes less stable relative to the states one higher and one lower, it undergoes disproportionation.

Example 1 — Manganese(VI) in acidic solution:

MnO_4^{2-} (manganate, Mn = +6) disproportionates in acid to give permanganate Mn(+7) and MnO_2 Mn(+4):

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

(Mn goes from +6 -> +7 (oxidised) and +6 -> +4 (reduced))

Example 2 — Copper(I) in aqueous solution:

Cu^+ (cuprous, +1) is unstable in aqueous solution and disproportionates into Cu^{2+} (+2) and Cu^0 (0):

$2\ Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$

(Cu goes from +1 -> +2 (oxidised) and +1 -> 0 (reduced))

The $E°(Cu^+/Cu)$ = +0.52V and $E°(Cu^{2+}/Cu^+)$ = +0.16V; the cell E° for the disproportionation is +0.52 - 0.16 = +0.36V > 0, so the reaction is spontaneous.

Answer: Disproportionation occurs when a species in one oxidation state simultaneously oxidises and reduces itself to give products in higher and lower oxidation states. Example 1: $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ ($Mn^{6+} \rightarrow Mn^{7+}$ and Mn^{4+}). Example 2: $2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$ ($Cu^+ \rightarrow Cu^{2+}$ and Cu^0).

Q23 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

SOLUTION

Copper (Cu, Z=29) exhibits the +1 oxidation state most frequently among the first series of transition metals.

Reason:
Copper has the electronic configuration [Ar] $3d^{10}$ $4s^1$ (not [Ar] $3d^9$ $4s^2$ as expected from the aufbau principle). When Cu loses one electron ($4s^1$), it gives Cu^+ with the configuration [Ar] $3d^{10}$ — a completely filled d subshell. This d^{10} configuration is exceptionally stable due to:
1. Completely filled 3d subshell gives maximum exchange energy
2. Spherically symmetric electron distribution
3. The closed-shell d^{10} configuration is inherently stable

Although Cu^+ is unstable in aqueous solution (disproportionates: $2Cu^+ \rightarrow Cu + Cu^{2+}$), it is stable in solid compounds such as CuCl, CuBr, CuI, and Cu_2O, as well as in complex compounds like $[Cu(CN)_2]^-$.

No other metal in the first transition series as readily forms and stabilises the +1 state: other M^+ ions would have partially filled d subshells which confer no particular extra stability.

Answer: Copper (Cu) most frequently exhibits +1 oxidation state. Cu has configuration [Ar] $3d^{10}$ $4s^1$; losing $4s^1$ gives Cu^+ with the stable, completely filled d^{10} configuration ([Ar] $3d^{10}$). This filled subshell has extra stability. Cu^+ is stable in solid compounds (CuCl, CuI, Cu_2O) and complexes like $[Cu(CN)_2]^-$, though it disproportionates in aqueous solution.

Q24 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?

SOLUTION

For 3+ ions of first row transition metals, 4s electrons are lost first, then 3d electrons are removed to form the 3+ ion.

Mn^{3+} (Z=25): Mn = [Ar] $3d^5$ $4s^2$. Mn^{3+} loses $4s^2$ and one 3d electron -> [Ar] $3d^4$.
$3d^4$ orbital occupancy (by Hund's rule): each of the first 4 orbitals gets one electron (all 4 spin-up)
Unpaired electrons = 4

mu = sqrt(4 x 6) = sqrt(24) = 4.90 BM

Cr^{3+} (Z=24): Cr = [Ar] $3d_5$ $4s_1$. Cr^{3+} loses $4s_1$ and two 3d electrons -> [Ar] $3d_3$.
$3d_3$ orbital occupancy: three orbitals with one electron each
Unpaired electrons = 3
mu = sqrt(3 x 5) = sqrt(15) = 3.87 BM

V^{3+} (Z=23): V = [Ar] $3d_3$ $4s_2$. V^{3+} loses $4s_2$ and one 3d electron -> [Ar] $3d_2$.
$3d_2$ orbital occupancy: two orbitals with one electron each
Unpaired electrons = 2
mu = sqrt(2 x 4) = sqrt(8) = 2.83 BM

Ti^{3+} (Z=22): Ti = [Ar] $3d_2$ $4s_2$. Ti^{3+} loses $4s_2$ and one 3d electron -> [Ar] $3d_1$.
$3d_1$ orbital occupancy: one orbital with one electron
Unpaired electrons = 1
mu = sqrt(1 x 3) = sqrt(3) = 1.73 BM

Most stable in aqueous solution:
Cr^{3+} is the most stable in aqueous solution. It has the d_3 configuration, which corresponds to a half-filled t_2g level in an octahedral environment (crystal field stabilisation energy is maximum for d_3 in strong fields). $E°(Cr^{3+}/Cr^{2+})$ = -0.41V, meaning Cr^{3+} strongly resists reduction, confirming its high stability.

Answer: Mn^{3+} (d_4): 4 unpaired electrons, mu = 4.90 BM. Cr^{3+} (d_3): 3 unpaired electrons, mu = 3.87 BM. V^{3+} (d_2): 2 unpaired electrons, mu = 2.83 BM. Ti^{3+} (d_1): 1 unpaired electron, mu = 1.73 BM. Most stable in aqueous solution: Cr^{3+} (d_3 configuration with maximum t_2g CFSE and very negative E° for Cr^{3+}/Cr^{2+} reduction).

Q25 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) Lowest oxide is basic, highest oxide is amphoteric/acidic:
In the lowest oxidation state, the metal has low charge and large ionic radius, so it behaves as a cation (M^n+) in an ionic metal oxide. These ionic oxides dissolve in acid to give metal salts: basic character.
Example: MnO (Mn^{2+}) is basic; dissolves in H_2SO_4 to give $MnSO_4$.
In the highest oxidation state, the metal has high charge density and the

metal-oxygen bonding becomes more covalent. High-valent metal in oxide behaves as acidic anhydride.
Example: CrO_3 (Cr^{6+}) is acidic — dissolves in NaOH; V_2O_5 (V^{5+}) is amphoteric — dissolves in both acid and alkali; Mn_2O_7 (Mn^{7+}) is a covalent acidic oil giving $HMnO_4$.

(ii) Highest oxidation state in oxides and fluorides:
Oxygen and fluorine are the most electronegative elements and also the smallest. They can:
- Stabilise higher oxidation states through strong ionic lattice energies (F^- forms ionic compounds with high lattice energy for smaller metal cations at high oxidation state)
- Form strong covalent bonds (O forms pi bonds via ppi-dpi overlap, allowing transfer of more electron density to the metal)
- Being small, multiple O or F atoms can coordinate around the metal without steric crowding
Example: Mn forms MnF_4 (highest fluoride) and Mn_2O_7 (highest oxide, +7 state); CrF_6 (Cr^{6+}), V_2O_5 (V^{5+}). In contrast, heavier halides (Cl, Br, I) are larger and cannot stabilise high oxidation states.

(iii) Highest oxidation state in oxoanions:
Oxygen is the most electronegative element and can form strong pi bonds with metals via ppi-dpi overlap. In tetrahedral oxoanions, each oxygen forms a double bond with the metal, allowing maximum electron withdrawal from the metal and maximum oxidation state to be achieved.
The high charge (electronegativity) of oxygen atoms stabilises high oxidation state metal centres.
Example: VO_4^{3-} (V^{5+}), CrO_4^{2-} (Cr^{6+}), MnO_4^- (Mn^{7+}) — each exhibits the maximum oxidation state in the tetrahedral oxoanion. In MnO_4^-, each O forms a pi bond with Mn(+7) through ppi-dpi overlap.

Answer: (i) Lowest oxide is ionic with low-charge metal cation — behaves as basic (e.g., MnO basic, dissolves in acid). Highest oxide has high-charge metal with covalent character — acidic or amphoteric (e.g., Mn_2O_7 acidic, V_2O_5 amphoteric). (ii) O and F are most electronegative and smallest, giving strong ionic lattice energies or strong covalent/pi bonds that stabilise the highest oxidation state (e.g., MnF_4, CrF_6, Mn_2O_7). (iii) Oxygen forms multiple (pi) bonds with metals via ppi-dpi overlap in tetrahedral oxoanions, withdrawing maximum electron density and stabilising the highest oxidation state (e.g., MnO_4^- has Mn^{7+}).

Q26 Indicate the steps in the preparation of: (i) $K_2Cr_2O_7$ from chromite ore. (ii) $KMnO_4$ from pyrolusite ore.

SOLUTION

(i) Preparation of $K_2Cr_2O_7$ from chromite ore ($FeCr_2O_4$):

Step 1 — Fusion with Na_2CO_3 in air:
$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \rightarrow 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$
Product: sodium chromate (Na_2CrO_4, yellow solution)

Step 2 — Acidification of Na_2CrO_4:
$2\ Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
(Or ionic: $2\ CrO_4^{2-} + 2\ H^+ \rightarrow Cr_2O_7^{2-} + H_2O$)
$Na_2Cr_2O_7$ crystallises from solution (orange crystals).

Step 3 — Treatment with KCl:
$Na_2Cr_2O_7 + 2\ KCl \rightarrow K_2Cr_2O_7 + 2\ NaCl$
$K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$ and crystallises out as orange crystals.

(ii) Preparation of $KMnO_4$ from pyrolusite ore (MnO_2):

Step 1 — Alkaline fusion of MnO_2:
MnO_2 is fused with KOH in the presence of air (or KNO_3 as oxidant) at high temperature:
$2\ MnO_2 + 4\ KOH + O_2 \rightarrow 2\ K_2MnO_4 + 2\ H_2O$
Product: potassium manganate (K_2MnO_4, dark green)

Step 2 — Electrolytic (or chemical) oxidation of K_2MnO_4:
Commercially, K_2MnO_4 is oxidised to $KMnO_4$ by electrolysis in alkaline solution:
$MnO_4^{2-} \rightarrow MnO_4^- + e^-$ (at anode)
Alternatively, in acidic/neutral solution, K_2MnO_4 disproportionates:
$3\ MnO_4^{2-} + 4\ H^+ \rightarrow 2\ MnO_4^- + MnO_2 + 2\ H_2O$

$KMnO_4$ crystallises as dark purple crystals.

Answer: (i) $K_2Cr_2O_7$: (1) Fuse $FeCr_2O_4 + Na_2CO_3 + air \rightarrow Na_2CrO_4$; (2) acidify -> $Na_2Cr_2O_7$; (3) treat with KCl -> $K_2Cr_2O_7$ crystallises. (ii) $KMnO_4$: (1) Fuse $MnO_2 + KOH + O_2 \rightarrow K_2MnO_4$ (green); (2) electrolytic oxidation of $MnO_4^{2-} \rightarrow MnO_4^-$ (or disproportionation in acid: $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$) -> $KMnO_4$ crystallises (purple).

Q27 What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

SOLUTION

Alloys are homogeneous solid mixtures (blends) of two or more metals (or a metal with a non-metal), prepared by mixing the molten components and allowing them to solidify together. Alloys may be homogeneous solid solutions in which atoms of one metal are randomly distributed among atoms of the other metal. They form when metals have similar atomic radii (within ~15%) and similar electronic characteristics.

Important alloy containing lanthanoid metals:
Mischmetall (also called mischmetal or mixed metal alloy)

Composition: ~95% lanthanoid metals (mixture of Ce, La, Nd, Pr, and other lanthanoids) + ~5% iron (Fe) + traces of sulfur (S), carbon (C), calcium (Ca), and aluminum (Al).

Uses of mischmetall:
1. Used in production of alloy steels for plates and pipes (gives high strength).
2. Mixed into Mg-based alloys to produce bullets, shells, and lighter flints.
3. The most familiar everyday use is as lighter flints (when struck, mischmetall gives hot sparks due to its pyrophoric nature).
4. Mixed oxides of lanthanoids (from mischmetall) are used as catalysts in petroleum cracking.
5. Individual lanthanoid oxides are used as phosphors in television screens and fluorescent surfaces.

Answer: Alloys are homogeneous solid mixtures of metals formed when components with similar atomic radii are melted together and solidified. Important lanthanoid alloy: Mischmetall — ~95% lanthanoid metals (Ce, La, etc.) + ~5% Fe + traces of S, C, Ca, Al. Uses: alloy steel production for plates/pipes, Mg-based alloy for bullets and shells, lighter flints (pyrophoric property), and as catalyst in petroleum cracking.

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.

SOLUTION

Inner transition elements are the f-block elements in which the last electron enters the f orbitals of the antepenultimate (third-from-outer) shell. They are placed in a separate two-row panel at the bottom of the periodic table.

There are two series:

- Lanthanoids (4f series): Ce to Lu, Z = 58 to 71 (14 elements); often La (Z=57) is included
- Actinoids (5f series): Th to Lr, Z = 90 to 103 (14 elements); often Ac (Z=89) is included

Now examining the given atomic numbers:

29 — Cu (Copper), Z=29: 3d transition metal (1st series), NOT an inner transition element.

59 — Pr (Praseodymium), Z=59: belongs to lanthanoid series (Z=58-71). YES, inner transition element.

74 — W (Tungsten), Z=74: 5d transition metal (3rd transition series, between lanthanoids and later 5d elements). NOT an inner transition element.

95 — Am (Americium), Z=95: belongs to actinoid series (Z=90-103). YES, inner transition element.

102 — No (Nobelium), Z=102: belongs to actinoid series (Z=90-103). YES, inner transition element.

104 — Rf (Rutherfordium), Z=104: 6d transition metal (4th series, starts at Z=104 after actinoids end at Z=103). NOT an inner transition element.

Answer: Inner transition elements are f-block elements (lanthanoids Z=58-71 and actinoids Z=90-103) in which the last electron enters the 4f or 5f orbital. From the given list: 59 (Pr — lanthanoid) ✓, 95 (Am — actinoid) ✓, and 102 (No — actinoid) ✓ are inner transition elements. 29 (Cu — 3d series), 74 (W — 5d series), and 104 (Rf — 6d series) are NOT inner transition elements.

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.

SOLUTION

The lanthanoids show predominantly the +3 oxidation state throughout the series, making their chemistry relatively smooth and predictable. In contrast, the actinoids show a wide and irregular range of oxidation states, especially in the early members.

Reasons for complexity in actinoids:
1. The 5f, 6d, and 7s orbitals are all close in energy, so more electrons from different subshells are available for bonding.
2. 5f orbitals are not as deeply buried as 4f orbitals; 5f electrons can participate in bonding to a far greater extent.
3. Many actinoids are radioactive (especially from Es onwards, with very short half-lives), making their study experimentally difficult.

Examples from oxidation states:
- Ac: only +3 (similar to lanthanoids)
- Th (Z=90): mainly +4 (d_0 product); +3 is rare
- Pa (Z=91): +4 and +5 are common
- U (Z=92): shows +3, +4, +5, and +6 (UO_2^{2+}, the uranyl ion, is prominent)
- Np (Z=93): shows +3, +4, +5, +6, and +7
- Pu (Z=94): shows +3, +4, +5, +6, and +7
- Am, Cm onwards: predominantly +3, becoming more lanthanoid-like

Comparison: Lanthanoids from La to Lu show consistently +3 (with only +2 for Eu, Yb and +4 for Ce, Tb). The actinoids, especially Pa through Am, show 4-5 different oxidation states each, making a group-wide summary of their chemistry far less straightforward.

Answer: Actinoid chemistry is irregular because 5f, 6d, and 7s levels have comparable energies, enabling multiple electrons to participate in bonding. Examples: Th(+4 mainly), Pa(+4,+5), U(+3 to +6), Np(+3 to +7), Pu(+3 to +7). Lanthanoids show consistently +3 (rare +2 or +4 only). Radioactivity of heavier actinoids further complicates study. Hence actinoid chemistry has no single oxidation state trend, unlike the smooth +3 dominance of lanthanoids.

Q30 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

The last element in the actinoid series is Lawrencium (Lr), atomic number Z = 103.

Electronic configuration:
Lr: [Rn] $5f_{14}$ $6d_1$ $7s_2$
(The 5f subshell is completely filled with 14 electrons, one electron in 6d, and two in 7s. Some sources also write [Rn] $5f_{14}$ $7s_2$ $7p_1$ depending on quantum chemical calculations, but NCERT uses [Rn] $5f_{14}$ $6d_1$ $7s_2$.)

Possible oxidation state:
Since Lr has completely filled $5f_{14}$ subshell (analogous to Lu in the lanthanoid series with $4f_{14}$), the most stable oxidation state is +3.
In the +3 state, Lr^{3+} has configuration [Rn] $5f_{14}$ — the completely filled and stable $5f_{14}$ configuration is retained.
Loss of the $6d_1$ and $7s_2$ electrons (3 electrons total) gives the +3 ion.
The +3 state is consistent with the trend observed for heavier actinoids (Fm, Md, No, Lr) which all predominantly show +3, behaving similarly to lanthanoids.
No is unusual in showing +2 (as No^{2+} has the stable $5f_{14}$ configuration like Yb^{2+} with $4f_{14}$); Lr returns to +3.

Answer: Last actinoid: Lawrencium (Lr), Z=103. Electronic configuration: [Rn] $5f_{14}$ $6d_1$ $7s_2$. The most stable and expected oxidation state is +3. In Lr^{3+}, the stable completely filled $5f_{14}$ subshell is retained (by losing $6d_1$ and $7s_2$ electrons). +3 is consistent with the trend of heavier actinoids.

Q31 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 (Cerium), Z = 58.

Electronic configuration of Ce (neutral atom):
Ce: [Xe] $4f_1$ $5d_1$ $6s_2$

Formation of Ce^{3+}:
Ce^{3+} is formed by removal of 3 electrons. The $6s_2$ and $5d_1$ electrons are removed first (outermost).
Ce^{3+}: [Xe] $4f_1$

Applying Hund's rule to Ce^{3+} ([Xe] $4f_1$):
The 4f subshell has 7 orbitals. With only 1 electron, Hund's rule places it in one 4f orbital with spin up (+1/2).
Configuration: $4f^1$ — one electron in one 4f orbital, all other 4f orbitals empty.
Number of unpaired electrons n = 1.

Magnetic moment calculation (spin-only formula):
mu = sqrt[n(n+2)] BM
mu = sqrt[1 x (1+2)] BM
mu = sqrt[1 x 3] BM
mu = sqrt(3) BM
mu = 1.73 BM

Answer: Ce (Z=58): [Xe] $4f_1$ $5d_1$ $6s_2$. Ce^{3+} loses $6s_2$ and $5d_1$ -> configuration [Xe] $4f_1$. By Hund's rule: 1 unpaired electron in the 4f orbital. Spin-only magnetic moment: mu = sqrt(1 x 3) = 1.73 BM.

Q32 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.

SOLUTION

Lanthanoids exhibiting +4 oxidation state:

1. Cerium (Ce, Z=58): Ce = [Xe] $4f_1$ $5d_1$ $6s_2$. Ce^{4+} gives [Xe] — the noble gas configuration (f_0, empty f subshell). The extra stability of the completely empty f subshell (f_0) drives the formation of +4 state.

2. Terbium (Tb, Z=65): Tb = [Xe] $4f^9\ 6s^2$. Tb^{4+} gives [Xe] $4f^7$ — the half-filled f^7 configuration, which has extra stability due to maximum exchange energy. This drives +4 state in Tb (mainly in the oxide TbO_2).

3. Praseodymium (Pr, Z=59), Neodymium (Nd, Z=60), Dysprosium (Dy, Z=66) also exhibit +4 state but only in their oxides (MO_2), not commonly in aqueous solution.

Lanthanoids exhibiting +2 oxidation state:

1. Europium (Eu, Z=63): Eu = [Xe] $4f^7\ 6s^2$. Eu^{2+} loses only $6s^2$ electrons and retains [Xe] $4f^7$ — the half-filled f subshell with maximum exchange energy and extra stability.

2. Ytterbium (Yb, Z=70): Yb = [Xe] $4f^{14}\ 6s^2$. Yb^{2+} loses $6s^2$ electrons only, giving [Xe] $4f^{14}$ — the completely filled f subshell with extra stability.

3. Samarium (Sm, Z=62): Sm = [Xe] $4f^6\ 6s^2$. Sm^{2+} = [Xe] $4f^6$ (slightly less stable; Sm^{2+} is a reducing agent).

Correlation with electronic configurations:
The formation of +4 or +2 states arises from the extra stability of f^0 (empty), f^7 (half-filled), and f^{14} (completely filled) f subshells. Any configuration that can attain one of these three by losing or gaining electrons will show anomalous +4 or +2 states.

Answer: +4 state: Ce (Ce^{4+} = [Xe], f^0), Tb (Tb^{4+} = $[Xe]_4f^7$, half-filled), Pr, Nd, Dy (in oxides). +2 state: Eu (Eu^{2+} = $[Xe]_4f^7$, half-filled), Yb (Yb^{2+} = $[Xe]_4f^{14}$, fully filled), Sm. Correlation: deviations from +3 are driven by extra stability of f^0, f^7 (half-filled), and f^{14} (completely filled) f subshell configurations.

Q33 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: General outer configuration [Xe] $4f^{1\text{-}14}\ 5d^{0\text{-}1}\ 6s^2$. The 4f orbitals are deeply buried inside the atom (shielded by outer shells), so 4f electrons are largely non-bonding. There are fewer exceptions to the 4f filling order.
Actinoids: General outer configuration [Rn] $5f^{1\text{-}14}\ 6d^{0\text{-}2}\ 7s^2$. The 5f orbitals are not as deeply buried as 4f — they extend further and are more accessible for

bonding. The 5f, 6d, and 7s energy levels are close, leading to more irregularities in electron filling and many more exceptions to expected configurations.

(ii) Oxidation States:
Lanthanoids: The dominant oxidation state is +3 throughout the series. Occasional +2 (Eu, Yb, Sm) and +4 (Ce, Tb in particular) are stabilised by f^0, f^7, f^{14} configurations. Range: +2, +3, +4 only.
Actinoids: Show a much wider and variable range. Early actinoids (Pa to Am) show many oxidation states: e.g., U shows +3 to +6; Np and Pu show +3 to +7. This is because 5f, 6d, and 7s levels are comparable in energy, so many electrons participate in bonding. Later actinoids (Cm to Lr) are predominantly +3, becoming more lanthanoid-like.

(iii) Chemical Reactivity:
Lanthanoids: Earlier members (La, Ce, Pr) are quite reactive — react with water (slowly), dilute acids, and burn in air. React with halogens, nitrogen, carbon at elevated temperatures to form halides, nitrides, and carbides. Reactivity decreases across the series; later members (Lu) are less reactive.
Actinoids: Generally more reactive than lanthanoids, especially when finely divided. React with boiling water producing oxide/hydride mixtures, react with most non-metals at moderate temperatures. HCl attacks all actinoids; HNO_3 forms protective oxide films. All actinoids are radioactive, with heavier members having very short half-lives, greatly complicating their chemistry.
Magnetic behaviour: Actinoids have more complex magnetic properties than lanthanoids due to greater involvement of 5f electrons in bonding (and orbital contributions to magnetic moment are not as quenched as in 3d elements).

Answer: (i) Config: lanthanoids fill 4f (buried, non-bonding); actinoids fill 5f (more exposed, can bond), more configuration irregularities. (ii) Oxidation states: lanthanoids mainly +3 (rare +2/+4 from $f^0/f^7/f^{14}$ stability); actinoids show +3 to +7 in early members (5f, 6d, 7s energies comparable), converging to +3 for later actinoids. (iii) Reactivity: actinoids are generally more reactive; all are radioactive. Lanthanoid reactivity decreases across the series; early members react like alkaline earths.

Q34 Write the electronic configurations of the elements with the atomic numbers 61, 91, 101, and 109.

SOLUTION

Z = 61 — Promethium (Pm), a lanthanoid (Z=57-71):
Core: [Xe] (Z=54), then 4f electrons fill from Ce (Z=58).
Pm: [Xe] $4f_5$ $6s_2$

Z = 91 — Protactinium (Pa), an actinoid (Z=89-103):
Core: [Rn] (Z=86)
Pa: [Rn] $5f_2$ $6d_1$ $7s_2$
(Pa has one 6d electron because 5f and 6d are close in energy at the beginning of actinoid series)

Z = 101 — Mendelevium (Md), an actinoid:
Core: [Rn] (Z=86), then fill 5f from Th (Z=90).
Md: [Rn] $5f_{13}$ $7s_2$

Z = 109 — Meitnerium (Mt), a 6d transition metal (4th series):
Core: [Rn] (Z=86), then $5f_{14}$ (fills from Th to Lr), then 6d series starts at Rf (Z=104).
Configuration after [Rn]: $5f_{14}$ + filling 6d from Rf(104):
Rf: $6d_2$, Db: $6d_3$, Sg: $6d_4$, Bh: $6d_5$, Hs: $6d_6$, Mt: $6d_7$
Mt: [Rn] $5f_{14}$ $6d_7$ $7s_2$

Answer: Z=61 (Pm): [Xe] $4f_5$ $6s_2$. Z=91 (Pa): [Rn] $5f_2$ $6d_1$ $7s_2$. Z=101 (Md): [Rn] $5f_{13}$ $7s_2$. Z=109 (Mt): [Rn] $5f_{14}$ $6d_7$ $7s_2$.

Q35 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.

SOLUTION

(i) Electronic configurations:
First series (3d): Configuration (n-1)d_1-10 ns_1-2 with outer 3d. Exceptions in Cr ([Ar]$_3d_5$ $4s_1$) and Cu ([Ar]$_3d_{10}$ $4s_1$) due to half-filled and fully filled d stability.
Second series (4d): More exceptions to expected filling — Nb, Mo, Ru, Rh, Pd show irregular 4d/5s distributions. Pd has the unusual $4d_{10}$ $5s_0$ configuration.
Third series (5d): Also shows exceptions. Pt has $5d_9$ $6s_1$. The 5d orbitals are more

diffuse and available for bonding.

(ii) Oxidation states:
First series: Shows variable oxidation states but the highest states (above +4) are less stable for later elements. Cr(VI) is strongly oxidising; Fe does not exceed +3 in simple oxides.
Second and third series: Higher oxidation states are MORE stable. Mo(VI) and W(VI) are stable (unlike Cr(VI) which is oxidising); Ru and Os can reach +8 (RuO_4, OsO_4). The heavier congeners preferentially form higher oxidation states due to better shielding of the d electrons.

(iii) Ionisation enthalpies:
First series: Lower ionisation enthalpies — easier to ionise.
Second and third series: Higher ionisation enthalpies due to greater nuclear charge and more diffuse d orbitals that are less effectively shielded. Third series metals have ionisation enthalpies comparable to second series (due to lanthanoid contraction causing similar effective nuclear charge).

(iv) Atomic sizes:
First to second series (3d->4d): Atomic radii INCREASE significantly (one additional shell is added).
Second to third series (4d->5d): Atomic radii remain virtually the same, despite addition of another shell. This is because the lanthanoid contraction (filling of 4f orbitals before 5d) compensates for the expected increase in size.
Example: Zr (160 pm) ≈ Hf (159 pm); Nb (143 pm) ≈ Ta (143 pm).
Consequence: 4d and 5d congeners have almost identical atomic radii, which is why they have very similar chemistry and are difficult to separate.

Answer: (i) Configurations: more exceptions in 2nd/3rd series (e.g., Pd=$4d_{10}$ $5s_0$); 4f filled before 5d in 3rd series. (ii) Oxidation states: higher states more stable in 2nd/3rd series (W(VI), Mo(VI) stable; Ru, Os reach +8); 1st series Cr(VI) is oxidising. (iii) Ionisation enthalpies: increase from 1st to 2nd/3rd series; 2nd and 3rd are comparable due to lanthanoid contraction. (iv) Atomic sizes: increase from 1st to 2nd series; nearly identical from 2nd to 3rd (lanthanoid contraction offsets the expected increase); e.g., Zr (160 pm) ≈ Hf (159 pm).

Q36 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

For transition metal ions, ns electrons are lost first, then (n-1)d electrons.
All ions below are in octahedral environment (hydrated, [M(H₂O)₆]^n+). In octahedral field, the 5 d orbitals split into t_{2g} (3 lower-energy orbitals) and eg (2 higher-energy orbitals).
For first-row transition metals with weak-field ligands (H_2O is weak field), HIGH SPIN configurations apply.

Ti^{2+} (Z=22): Ti=[Ar]$3d_2$ $4s_2$, loses $4s_2$ -> $3d_2$. 3d electrons = 2.
Octahedral (high spin): t_{2g}^2 eg^0 — 2 unpaired in t_{2g}. |↑|↑|_| |_|_|

V^{2+} (Z=23): V=[Ar]$3d_3$ $4s_2$, loses $4s_2$ -> $3d_3$. 3d electrons = 3.
Octahedral (high spin): t_{2g}^3 eg^0 — 3 unpaired in t_{2g} (half-filled t_{2g}). |↑|↑|↑| |_|_|

Cr^{3+} (Z=24): Cr=[Ar]$3d_5$ $4s_1$, Cr^{3+} loses $4s_1$+two 3d -> $3d_3$. 3d electrons = 3.
Octahedral (high spin): t_{2g}^3 eg^0 — 3 unpaired. |↑|↑|↑| |_|_|

Mn^{2+} (Z=25): Mn=[Ar]$3d_5$ $4s_2$, loses $4s_2$ -> $3d_5$. 3d electrons = 5.
Octahedral (high spin): t_{2g}^3 eg^2 — 5 unpaired (half-filled). |↑|↑|↑| |↑|↑|

Fe^{2+} (Z=26): Fe=[Ar]$3d_6$ $4s_2$, loses $4s_2$ -> $3d_6$. 3d electrons = 6.
Octahedral (high spin, H_2O weak field): t_{2g}^4 eg^2 — 4 unpaired. |↑↓|↑|↑| |↑|↑|

Fe^{3+} (Z=26): Fe=[Ar]$3d_6$ $4s_2$, Fe^{3+} loses $4s_2$+one 3d -> $3d_5$. 3d electrons = 5.
Octahedral (high spin): t_{2g}^3 eg^2 — 5 unpaired. |↑|↑|↑| |↑|↑|

Co^{2+} (Z=27): Co=[Ar]$3d_7$ $4s_2$, loses $4s_2$ -> $3d_7$. 3d electrons = 7.
Octahedral (high spin): t_{2g}^5 eg^2 — 3 unpaired. |↑↓|↑↓|↑| |↑|↑|

Ni^{2+} (Z=28): Ni=[Ar]$3d_8$ $4s_2$, loses $4s_2$ -> $3d_8$. 3d electrons = 8.
Octahedral (high spin): t_{2g}^6 eg^2 — 2 unpaired. |↑↓|↑↓|↑↓| |↑|↑|

Cu^{2+} (Z=29): Cu=[Ar]$3d_{10}$ $4s_1$, Cu^{2+} loses $4s_1$+one 3d -> $3d_9$. 3d electrons = 9.
Octahedral: t_{2g}^6 eg^3 — 1 unpaired. |↑↓|↑↓|↑↓| |↑↓|↑|

Answer: Ti^{2+} ($3d_2$, t_{2g}^2 eg^0, 2 unpaired); V^{2+} ($3d_3$, t_{2g}^3 eg^0, 3 unpaired); Cr^{3+} ($3d_3$, t_{2g}^3 eg^0, 3 unpaired); Mn^{2+} ($3d_5$, t_{2g}^3 eg^2, 5 unpaired); Fe^{2+} ($3d_6$, t_{2g}^4 eg^2, 4 unpaired, high spin); Fe^{3+} ($3d_5$, t_{2g}^3 eg^2, 5 unpaired); Co^{2+} ($3d_7$, t_{2g}^5 eg^2, 3 unpaired); Ni^{2+} ($3d_8$, t_{2g}^6 eg^2, 2 unpaired); Cu^{2+} ($3d_9$, t_{2g}^6 eg^3, 1 unpaired). All are high-spin (weak-field H_2O ligands).

Q37 Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

SOLUTION

The statement is correct. The first series (3d) transition metals differ significantly from the heavier 4d and 5d series in several key properties:

1. Atomic and ionic sizes:
First series: smaller atomic and ionic radii.
Second series: larger (one additional shell). Third series: nearly same as second series (lanthanoid contraction keeps 5d series radii similar to 4d series).
Consequence: heavier metals form more metal-metal bonds and more stable metal carbonyl and organometallic compounds.

2. Oxidation states:
First series: higher oxidation states (above +4) are often unstable or strongly oxidising [e.g., Cr(VI) is a strong oxidant, Fe(VI) is very unstable].
Heavier series: higher oxidation states are more stable [Mo(VI) and W(VI) are stable; Ru and Os can reach +8 as OsO_4 and RuO_4].

3. Ionisation enthalpies:
First series: generally lower than the second and third series.
Second and third series: higher ionisation enthalpies due to larger nuclear charge without proportional increase in shielding.

4. Colour and spectral properties:
First series: vivid colours in many ions (due to d-d transitions with significant crystal field splitting).
Heavier series: crystal field splitting is larger (5d > 4d > 3d), so transitions may shift into the UV, giving different colours or more intense colours.

5. Magnetic properties:
First series: many ions are high-spin with multiple unpaired electrons.
Heavier series: often low-spin due to larger crystal field splitting, giving fewer unpaired electrons and diamagnetic or weakly paramagnetic behaviour.

6. Catalytic behaviour and complex formation:
Heavier transition metals form more stable complexes and have greater tendency for metal-metal bonding. Many industrial catalysts involve 4d and 5d metals (Pd, Pt, Rh, Ru).

7. Frequency of metal-metal bonds:

Heavier transition metals form multiple metal-metal bonds far more readily (higher enthalpy of atomisation).

In summary, the first series 3d metals are markedly different in size, oxidation state stability, magnetic properties, and complex formation behaviour compared to the heavier 4d and 5d series.

Answer: First-series (3d) metals differ from heavier (4d, 5d) series in: (1) smaller size (heavier series have larger radii, but 4d ~ 5d due to lanthanoid contraction); (2) lower stability of high oxidation states (Cr^{6+} is oxidising; Mo^{6+}, W^{6+} are stable); (3) often high-spin (heavier series are often low-spin — larger crystal field splitting); (4) less tendency to form metal-metal bonds; (5) lower ionisation enthalpies. The heavier transition metals show more metal-metal bonding, more stable high oxidation states, and different magnetic properties.

Q38 What can be inferred from the magnetic moment values of the following complex species? $K_4[Mn(CN)_6]$ (mu = 2.2 BM); $[Fe(H_2O)_6]^{2+}$ (mu = 5.3 BM); $K_2[MnCl_4]$ (mu = 5.9 BM)

SOLUTION

The spin-only magnetic moment formula: mu = sqrt[n(n+2)] BM, where n = number of unpaired electrons.
Key values: n=1: 1.73 BM; n=2: 2.83 BM; n=3: 3.87 BM; n=4: 4.90 BM; n=5: 5.92 BM.

$K_4[Mn(CN)_6]$ — mu = 2.2 BM:
Oxidation state of Mn: 4(+1) + Mn + 6(-1) = 0 -> Mn = +2. $Mn^{2+} = d_5$.
From mu = 2.2 BM, closest value is n=1 (calc. 1.73 BM). So approximately 1 unpaired electron.
CN^- is a strong-field ligand. For d_5 in a strong octahedral crystal field -> LOW SPIN -> $t_2g^5\ eg^0$ -> 1 unpaired electron.
Inference: $K_4[Mn(CN)_6]$ is a low-spin complex. Mn^{2+} is in +2 state; CN^- as strong-field ligand causes pairing of electrons, giving only 1 unpaired electron and mu ~ 1.73 BM (observed 2.2 BM, slightly higher due to some orbital contribution).

$[Fe(H_2O)_6]^{2+}$ — mu = 5.3 BM:
$Fe^{2+} = d_6$ (loses $4s_2$ from Fe = $[Ar]_3d_6\ 4s_2$).
From mu = 5.3 BM, closest value is n=4 (calc. 4.90 BM). So approximately 4 unpaired electrons.

H_2O is a weak-field ligand. For d_6 in weak octahedral field -> HIGH SPIN -> t_2g^4 eg^2 -> 4 unpaired electrons.
Inference: $[Fe(H_2O)_6]^{2+}$ is a high-spin complex. Fe^{2+} in +2 state; H_2O weak-field gives 4 unpaired electrons. The observed value (5.3 BM) is slightly higher than 4.90 BM due to some orbital angular momentum contribution.

$K_2[MnCl_4]$ — mu = 5.9 BM:
Oxidation state of Mn: 2(+1) + Mn + 4(-1) = 0 -> Mn = +2. Mn^{2+} = d_5.
From mu = 5.9 BM, this matches n=5 (calc. 5.92 BM). So 5 unpaired electrons.
Cl^- is a weak-field ligand. The complex $[MnCl_4]^{2-}$ is tetrahedral (4-coordinate).
For d_5 with weak-field tetrahedral -> HIGH SPIN -> all 5 d electrons are unpaired.
Inference: $K_2[MnCl_4]$ is a high-spin complex (tetrahedral). Mn^{2+} in +2 state; Cl^- weak-field gives 5 unpaired electrons. mu = 5.9 BM is consistent with n=5 (5.92 BM).

Answer: $K_4[Mn(CN)_6]$ (2.2 BM): Mn^{2+} (d_5) with strong-field CN^- -> low-spin t_2g^5 eg^0 -> 1 unpaired electron; mu calc = 1.73 BM (orbital contributions account for slightly higher observed value). $[Fe(H_2O)_6]^{2+}$ (5.3 BM): Fe^{2+} (d_6) with weak-field H_2O -> high-spin t_2g^4 eg^2 -> 4 unpaired electrons; mu calc = 4.90 BM. $K_2[MnCl_4]$ (5.9 BM): Mn^{2+} (d_5) with weak-field Cl^- in tetrahedral complex -> high-spin -> 5 unpaired electrons; mu calc = 5.92 BM (excellent agreement).