CLASS 12 CHEMISTRY NCERT SOLUTIONS

NCERT Solutions for Class 12 Chemistry Chapter 4: The d- and f-Block Elements – Free PDF Download

Chapter 4 covers the d- and f-Block Elements — electronic configuration and general trends of the first transition (3d) series, oxidation states, magnetic properties, catalytic behaviour, formation of coloured ions, interstitial compounds and alloys, preparation and reactions of potassium dichromate and potassium ...

Contents

Chapter 4 covers the **d- and f-Block Elements** — electronic configuration and general trends of the first transition (3d) series, oxidation states, magnetic properties, catalytic behaviour, formation of coloured ions, interstitial compounds and alloys, preparation and reactions of potassium dichromate and potassium permanganate, and the lanthanoids and actinoids (electronic configuration, oxidation states, lanthanoid contraction and its consequences). All 38 exercises (4.1–4.38) remain current under the 2026-27 syllabus — this chapter was not affected by the deletions that removed Surface Chemistry, Solid State, and the General Principles of Isolation of Elements. Each answer below is checked for chemical accuracy before publishing.

NCERT Exercise Solutions

4.1 Write the electronic configurations of the following ions: (i) Cr^{3+} (ii) Pm^{3+} (iii) Cu^{+} (iv) Ce^{4+} (v) Co^{2+} (vi) Lu^{2+} (vii) Mn^{2+} (viii) Th^{4+}.
Ans: (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].

4.2 Why are Mn^{2+} compounds more resistant to oxidation than Fe^{2+} compounds?
Ans: Mn^{2+} has the configuration $[Ar]3d^5$, a stable, exactly half-filled d-subshell. Oxidising it to Mn^{3+} ($3d^4$) disrupts this extra stability, so the process is energetically unfavourable. Fe^{2+} is $[Ar]3d^6$, and losing one electron gives Fe^{3+} ($3d^5$) — a more stable, half-filled configuration — so oxidation is comparatively easy for Fe^{2+} but resisted for Mn^{2+}.

4.3 The $E°(M^{2+}/M)$ value for copper is positive (+0.34V). Explain why Cu is the only metal in the first transition series showing a positive value.
Ans: The positive $E°(M^{2+}/M)$ for copper reflects the high energy needed to convert solid Cu into $Cu^{2+}(aq)$: copper has an unusually high enthalpy of atomisation (strong metallic bonding, since $3d^{10}4s^1$ allows extensive orbital overlap) combined with a relatively low hydration enthalpy for Cu^{2+} compared to other 3d ions. Since the overall enthalpy required to atomise and ionise the metal is not fully compensated by hydration energy, the process is endothermic overall — unlike the rest of the series, where hydration enthalpy is large enough to make $E°$ negative, so Cu does not readily displace H^+ from acids the way other first-series metals do.

4.4 To what extent do the electronic configurations decide the stability of oxidation states in the first series of transition elements? Illustrate with examples.
Ans: Electronic configuration is the primary factor. Elements whose atoms/ions can attain an empty, half-filled or fully-filled d-subshell by losing a particular number of electrons show that oxidation state as especially stable. For example, Mn ($[Ar]3d^5 4s^2$) can lose all 7 electrons to show its group oxidation state of +7 (as in MnO_4^-), but its most stable state is +2 ($3d^5$, half-filled). Similarly, Zn ($[Ar]3d^{10}4s^2$) shows only +2 because the $3d^{10}$ configuration is so stable that d-electrons never participate in bonding, while Sc shows only +3 ($3d^0$, empty and stable) despite having a $3d^1 4s^2$ ground state.

4.5 What may be the stable oxidation states of the transition elements with the following d-electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$?
Ans: $3d^3$ (V, $[Ar]3d^3 4s^2$): stable states +2, +3, +4, +5. $3d^5$ can be either Cr ($[Ar]3d^5 4s^1$: stable +3, +6) or Mn ($[Ar]3d^5 4s^2$: stable +2, +4, +6, +7). $3d^8$ (Ni, $[Ar]3d^8 4s^2$): stable +2 (rarely +3, +4). **$3d^4$ does not occur as a ground-state configuration for any first-series atom** — Cr is anomalously $[Ar]3d^5 4s^1$ rather than $[Ar]3d^4 4s^2$, so no stable oxidation state can be assigned to this configuration.

4.6 Name the oxometal anions of the first series of transition metals in which the metal exhibits an oxidation state equal to its group number.
Ans: **MnO_4^-** (permanganate; Mn in group 7, oxidation state +7) and **CrO_4^{2-}/$Cr_2O_7^{2-}$** (chromate/dichromate;

Cr in group 6, oxidation state +6).

4.7 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
Ans: **Lanthanoid contraction** is the steady, cumulative decrease in atomic and ionic radii of the lanthanoid elements (La to Lu) with increasing atomic number. It occurs because the 4f electrons being added shield the increasing nuclear charge only imperfectly (poor shielding of one 4f electron by another), so the effective nuclear charge experienced by outer electrons rises steadily, pulling the electron cloud inward. **Consequences:** (i) the atomic/ionic radii of the second (4d) and third (5d) transition series elements of a given group become nearly identical (e.g. Zr and Hf, Nb and Ta), making them very difficult to separate chemically; (ii) the basic strength of lanthanoid hydroxides decreases steadily from $La(OH)_3$ to $Lu(OH)_3$ as ionic size falls; (iii) it causes small but significant differences in properties among the lanthanoids themselves, useful in their separation.

4.8 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?
Ans: Transition elements are characterised by variable oxidation states, formation of coloured ions, paramagnetism, catalytic activity, and a tendency to form complexes and alloys; they are called “transition” elements because their properties are transitional between the highly reactive, electropositive s-block metals and the electronegative p-block elements. They are defined as elements having an **incompletely filled d-subshell in the ground state or in any one of their commonly occurring oxidation states**. **Zn, Cd and Hg** (group 12) have a fully-filled d^{10} configuration both as elements and in their common (+2) oxidation state, so they are not regarded as true transition elements.

4.9 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 oxidised. (iii) The d^1 configuration is very unstable in ions.
Ans: (i) $Cr^{2+}(3d^4) \rightarrow Cr^{3+}(3d^3, t_{2g}^3$, an extra-stable half-filled t_{2g} level) — so Cr^{2+} readily loses an electron, making it a strong **reducing** agent. $Mn^{3+}(3d^4) \rightarrow Mn^{2+}(3d^5$, fully half-filled, extra stable) — so Mn^{3+} readily gains an electron, making it a strong **oxidising** agent. (ii) In water, $Co^{2+}(3d^7)$ is more stable than $Co^{3+}(3d^6)$ on hydration-energy grounds, but strong-field complexing ligands (e.g. NH_3, CN^-) impose large crystal-field stabilisation on the low-spin d^6 Co^{3+} configuration (t_{2g}^6), which favours Co^{3+} enough to make oxidation of Co^{2+} to Co^{3+} spontaneous in their presence. (iii) A d^1 ion has just one electron beyond an empty, extra-stable d^0 shell, so it readily loses that electron (oxidising further, e.g. $Ti^{3+} \rightarrow Ti^{4+}$) to attain the more stable empty configuration, making d^1 species inherently unstable/easily oxidised.

4.10 What is meant by “disproportionation”? Give two examples of disproportionation reactions in aqueous solution.
Ans: **Disproportionation** is a redox reaction in which a species in one (intermediate) oxidation state is simultaneously oxidised and reduced, giving two different oxidation states of the same element as products. Examples: $\mathbf{3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O}$ (Mn(VI) disproportionates to Mn(VII) and Mn(IV)); and $\mathbf{2Cu^+ \rightarrow Cu^{2+} + Cu}$ (Cu(I) disproportionates to Cu(II) and Cu(0) in aqueous solution, since Cu^+ is thermodynamically unstable relative to Cu^{2+} and Cu metal in water).

4.11 Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?
Ans: **Copper (Cu)**. Its ground-state configuration is $[Ar]3d^{10}4s^1$, so losing the single 4s electron gives Cu^+ with a fully-filled, extra-stable $3d^{10}$ configuration, making the +1 state common for copper (e.g. Cu_2O, CuCl).

4.12 Calculate the “spin only” magnetic moment of M^{2+}(aq) ions (Z=27).
Ans: Z=27 is cobalt; Co^{2+} has the configuration $[Ar]3d^7$, giving **n=3 unpaired electrons** ($t_{2g}^5 e_g^2$ in a high-spin octahedral field). Spin-only magnetic moment $\mu = \sqrt{n(n+2)}$ BM $= \sqrt{(3 \times 5)} = \sqrt{15} \approx$ **3.87 BM**.

4.13 Explain why Cu^+ ion is not stable in aqueous solutions?
Ans: $Cu^+(aq)$ disproportionates spontaneously: **$2Cu^+(aq) \rightarrow Cu^{2+}(aq) + Cu(s)$**. Although Cu^+ ($3d^{10}$) has a stable filled d-subshell, the much higher hydration enthalpy of the smaller, more highly charged Cu^{2+} ion more than compensates for the loss of that extra stability, making $Cu^{2+}(aq)$ thermodynamically favoured over $Cu^+(aq)$.

4.14 Actinoid contraction is greater from element to element than lanthanoid contraction. Why?
Ans: Actinoid contraction arises from the imperfect shielding of one 5f electron by another, just as lanthanoid contraction arises from imperfect 4f-4f shielding. However, **5f orbitals shield the nuclear charge even more poorly than 4f orbitals** (5f orbitals are more diffuse and penetrate less effectively), so the effective nuclear charge experienced by outer electrons rises more sharply from one actinoid to the next, making the contraction per element larger than in the lanthanoids.

4.15 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.
Ans: Lanthanoids show an overwhelmingly uniform +3 oxidation state (with only occasional +2/+4 exceptions like Eu^{2+}, Ce^{4+}). Actinoids, by contrast, show a **much wider and less regular range of oxidation states** because their 5f, 6d and 7s orbital energies are very close, allowing more electrons to take part in bonding — e.g. uranium shows +3, +4, +5 and +6; neptunium and plutonium can reach +7 in some compounds. This irregular, element-dependent spread of oxidation states, together with the fact that all actinoids are radioactive (many with short half-lives, complicating systematic study), makes actinoid chemistry considerably less smooth/predictable than that of the lanthanoids.

4.16 Which is a stronger reducing agent, Cr^{2+} or Fe^{2+}, and why?
Ans: **Cr^{2+}** is the stronger reducing agent. $Cr^{2+}(3d^4) \rightarrow Cr^{3+}(3d^3$, an extra-stable, exactly half-filled t_{2g} level) is a favourable change, so Cr^{2+} readily loses an electron. $Fe^{2+}(3d^6) \rightarrow Fe^{3+}(3d^5$, also half-filled and stable) is also favourable, but the E° values ($Cr^{3+}/Cr^{2+} = -0.41V$ vs $Fe^{3+}/Fe^{2+} = +0.77V$) show oxidation of Cr^{2+} is thermodynamically far more favourable than that of Fe^{2+}.

4.17 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?
Ans: $Mn^{3+}(3d^4)$: **4** unpaired electrons. $Cr^{3+}(3d^3)$: **3** unpaired electrons. $V^{3+}(3d^2)$: **2** unpaired electrons. $Ti^{3+}(3d^1)$: **1** unpaired electron. **Cr^{3+}** is the most stable in aqueous solution, owing to its exactly half-filled, extra-stable t_{2g}^3 configuration and high crystal-field stabilisation/hydration energy.

4.18 Give examples and suggest reasons for the following features of transition metal chemistry: (i) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic. (ii) A transition metal exhibits higher oxidation states in oxides and fluorides. (iii) The highest oxidation state is exhibited in oxoanions of a metal.
Ans: (i) As the oxidation state of the metal rises, the metal-oxygen bond becomes progressively more covalent (ionic character falls), making higher oxides progressively more acidic — e.g. **MnO is basic, Mn_2O_3 is weakly basic/amphoteric, MnO_2 is amphoteric, and Mn_2O_7 is strongly acidic** (indeed a covalent, low-boiling liquid). (ii) Oxygen and fluorine, being the most electronegative and smallest elements, can stabilise the metal's highest oxidation states best — oxygen additionally can form pπ–dπ multiple bonds with the metal, giving added stability, e.g. **OsO_4 (+8), MnO_3F (+7)**. (iii) Oxoanions (e.g. **MnO_4^-, $Cr_2O_7^{2-}$**) let the metal reach its highest oxidation state because the small, highly electronegative, multiply-bonding oxygen atoms both withdraw electron density effectively and delocalise the resulting negative charge over the anion, stabilising the otherwise highly oxidising, highly charged metal centre.

4.19 Give reasons for the following: (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

compounds are generally good catalysts.
Ans: (i) Most transition metal ions have partially filled d-orbitals, so many of their electrons remain unpaired, giving rise to **paramagnetism**. (ii) Transition metals have a large number of unpaired electrons in both the (n−1)d and ns orbitals available for metallic bonding, giving **strong metal-metal bonding** and hence high enthalpies of atomisation. (iii) Partially filled d-orbitals allow **d-d electronic transitions**: an electron can absorb a specific wavelength of visible light to jump between split d-orbital energy levels (in the presence of ligands), and the complementary wavelength transmitted/reflected gives the compound its observed colour. (iv) Transition metals show **variable oxidation states** and can form unstable intermediate complexes with reactants, providing an alternative reaction pathway with lower activation energy; their large surface area (in finely divided/heterogeneous form) and ability to adsorb reactants (using vacant d-orbitals) further aid catalysis.

4.20 Compare the chemistry of the actinoids with that of the lanthanoids with special reference to: (i) electronic configuration (ii) oxidation states and (iii) chemical reactivity.
Ans: (i) **Electronic configuration:** Lanthanoids are $[Xe]4f^{1-14}5d^{0-1}6s^2$; actinoids are $[Rn]5f^{1-14}6d^{0-2}7s^2$ — actinoids show more irregularity since 5f, 6d and 7s energies are closer than the corresponding 4f, 5d, 6s energies in lanthanoids. (ii) **Oxidation states:** lanthanoids show mainly +3 (rarely +2 or +4); actinoids show a much wider range (+3 to +6, occasionally +7), since more of their outer electrons can take part in bonding. (iii) **Chemical reactivity:** early lanthanoids are fairly reactive (similar to calcium), with reactivity decreasing along the series as ionic size falls; actinoids are, in general, more reactive still, particularly the earlier members, and their chemistry is complicated by radioactivity, which lanthanoid chemistry does not have to contend with.

4.21 How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?
Ans: All three represent a transition metal in its highest (group) oxidation state (V: +5, Cr: +6, Mn: +7). As the oxidation state of the central metal rises across the series, the ion becomes progressively more strongly oxidising because it is progressively easier for the metal to be reduced (gain electrons) to a lower, more stable oxidation state — the ionisation energy trend and the increasing stability of the reduced products (V^{4+}, Cr^{3+}, Mn^{2+}, the last being an especially stable half-filled d^5 configuration) both favour reduction more strongly as the series progresses, so oxidising power increases from VO_2^+ to $Cr_2O_7^{2-}$ to MnO_4^-.

4.22 Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?
Ans: **Preparation:** the ore ($FeCr_2O_4$) is fused with sodium carbonate in free access of air: $\mathbf{4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2}$. The yellow sodium chromate solution is filtered and acidified to sodium dichromate: $\mathbf{2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O}$, and treated with KCl: $\mathbf{Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl}$, from which orange $K_2Cr_2O_7$ crystallises out on cooling (being less soluble than NaCl in cold water). **Effect of pH:** chromate and dichromate exist in a pH-dependent equilibrium, $\mathbf{2CrO_4^{2-}(yellow) + 2H^+ \rightleftharpoons Cr_2O_7^{2-}(orange) + H_2O}$; increasing the pH (making the solution more basic) shifts the equilibrium towards the yellow chromate ion, while decreasing pH (acidic conditions) favours the orange dichromate ion.

4.23 Write the ionic equations for the reactions of potassium dichromate solution with (i) iodide ions (ii) iron(II) ions (iii) H_2S, all in acidic medium.
Ans: (i) $\mathbf{Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2}$. (ii) $\mathbf{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}}$. (iii) $\mathbf{Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S}$.

4.24 Describe the oxidising action of potassium permanganate and write the ionic equations for its reactions with (i) iodide ion (ii) SO_2 and (iii) oxalic acid, in acidic solution.
Ans: In acidic medium, MnO_4^- is a powerful oxidising agent, being reduced to Mn^{2+}: $\mathbf{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}$. (i) $\mathbf{2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2}$. (ii)

$2MnO_4^- + 5SO_2 + 2H_2O \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 4H^+$. (iii) **$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$**.

4.25 Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions and (ii) oxalic acid?
Ans: **Preparation:** pyrolusite ore (MnO_2) is fused with KOH in the presence of an oxidising agent like KNO_3 or atmospheric O_2, giving dark green potassium manganate: **$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$**. This is then oxidised electrolytically (anodic oxidation) to purple permanganate: **$MnO_4^{2-} \rightarrow MnO_4^- + e^-$**, or disproportionates on acidification: **$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$**. (i) **$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$**. (ii) **$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$**.

4.26 How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.
Ans: Transition metals show oxidation states that generally differ from one another by **units of 1** (e.g. Fe^{2+}/Fe^{3+}, Cu^+/Cu^{2+}, Mn showing +2,+3,+4,+6,+7), because both the (n−1)d and ns electrons, having comparable energies, can be involved in bonding one at a time. Non-transition (main-group) elements typically show oxidation states differing by **units of 2** (e.g. Sn^{2+}/Sn^{4+}, Pb^{2+}/Pb^{4+}, Tl^+/Tl^{3+}), since their ns electron pair is usually lost or retained together (the “inert pair effect”).

4.27 Describe the variation in properties of the lanthanoids with respect to (i) ionic size and (ii) chemical reactivity.
Ans: (i) **Ionic size** decreases steadily and almost regularly from La^{3+} (largest) to Lu^{3+} (smallest) — this is the lanthanoid contraction, caused by imperfect 4f-4f shielding as nuclear charge increases. (ii) **Chemical reactivity** is high for the early members (La, Ce), comparable to that of calcium, and decreases steadily along the series with decreasing ionic size — the later, smaller lanthanoids are somewhat less reactive, though all are more electropositive/reactive than the transition metals proper.

4.28 Compare the general characteristics of the first series of transition elements with those of the second and third series metals in the same group, with special reference to (i) ionic radii (ii) oxidation states and (iii) chemical reactivity.
Ans: (i) **Ionic radii:** radii increase from the first (3d) to the second (4d) series, but due to lanthanoid contraction, the third (5d) series ions are almost the same size as the corresponding second-series ions rather than larger. (ii) **Oxidation states:** the heavier (4d, 5d) members show a wider range of oxidation states and greater stability of higher oxidation states than their 3d counterparts (e.g. Mo and W readily show +6, more so than Cr). (iii) **Chemical reactivity:** first-series elements tend to form more ionic compounds and are generally more reactive, while 4d/5d elements show a greater tendency to form metal-metal bonds/clusters and are typically less reactive, denser, and have higher melting points.

4.29 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 use the d-orbital splitting to account for the actual value of the “spin only” magnetic moment of each one of them.
Ans: Ti^{2+}: **$3d^2$** (t_{2g}^2, 2 unpaired, μ≈2.83 BM). V^{2+}: **$3d^3$** (t_{2g}^3, 3 unpaired, μ≈3.87 BM). Cr^{3+}: **$3d^3$** (t_{2g}^3, 3 unpaired, μ≈3.87 BM). Mn^{2+}: **$3d^5$** (high-spin $t_{2g}^3 e_g^2$, 5 unpaired, μ≈5.92 BM). Fe^{2+}: **$3d^6$** (high-spin $t_{2g}^4 e_g^2$, 4 unpaired, μ≈4.90 BM). Fe^{3+}: **$3d^5$** (high-spin, 5 unpaired, μ≈5.92 BM). Co^{2+}: **$3d^7$** (high-spin $t_{2g}^5 e_g^2$, 3 unpaired, μ≈3.87 BM). Ni^{2+}: **$3d^8$** ($t_{2g}^6 e_g^2$, 2 unpaired, μ≈2.83 BM). Cu^{2+}: **$3d^9$** ($t_{2g}^6 e_g^3$, 1 unpaired, μ≈1.73 BM). In each case, the number of unpaired electrons n (found from how the d-orbitals split into the lower t_{2g} and higher e_g sets and fill according to Hund’s rule) is used in the spin-only formula $\mu = \sqrt{n(n+2)}$ BM to obtain the value quoted.

4.30 Name the members of the lanthanoid series which are well known to exhibit +4 oxidation state besides the +3 state, and give reasons for this type of behaviour.
Ans: **Cerium (Ce)** and **terbium (Tb)** are the best-known examples. Ce^{4+} attains the empty, extra-stable **$[Xe]4f^0$** configuration, while Tb^{4+} attains the half-filled, extra-stable **$[Xe]4f^7$** configuration — in both cases,

losing a fourth electron leads to a specially stable f-configuration, making the +4 state accessible in addition to the usual +3.

4.31 What is meant by "actinoid contraction"? Why is it greater than the lanthanoid contraction?
Ans: **Actinoid contraction** is the steady decrease in atomic and ionic radii across the actinoid series (Th to Lr) with increasing atomic number, caused by imperfect shielding of the added 5f electrons by one another. It is **greater than lanthanoid contraction** because 5f orbitals are more diffuse/penetrate less effectively than 4f orbitals, so they shield the increasing nuclear charge even more poorly — the effective nuclear charge (and hence the contraction per element) rises more sharply across the actinoids.

4.32 Name the element that shows the greatest number of oxidation states among the actinoids, and write all of its oxidation states.
Ans: **Neptunium (Np)** and **Americium (Am)** are both well known for an especially wide spread, but **uranium (U)** is the most commonly cited textbook example, showing oxidation states of **+3, +4, +5 and +6** (with +6, as in UO_2^{2+}, being the most stable and important in its chemistry).

4.33 Compare the chemistry of actinoids with that of lanthanoids with special reference to oxidation states and chemical reactivity.
Ans: **Oxidation states:** lanthanoids show an overwhelmingly consistent +3 state (rarely +2/+4), while actinoids show a much broader, more irregular range (+3 to +6, occasionally +7), reflecting how close the 5f, 6d and 7s orbital energies are in the actinoids. **Chemical reactivity:** actinoids are, on the whole, more reactive than lanthanoids, especially the earlier members of the series, and their chemistry is further complicated by the fact that all actinoids are radioactive, several with short half-lives — a complication that plays no role in lanthanoid chemistry.

4.34 Write the electronic configurations of the elements with atomic numbers 61, 91, 101 and 109.
Ans: Z=61 (**Promethium, Pm**): $[Xe]4f^5 6s^2$. Z=91 (**Protactinium, Pa**): $[Rn]5f^2 6d^1 7s^2$. Z=101 (**Mendelevium, Md**): $[Rn]5f^{13} 7s^2$. Z=109 (**Meitnerium, Mt**): $[Rn]5f^{14} 6d^7 7s^2$.

4.35 Compare the general characteristics of the first series of the transition metals with those of the second and third series metals in general with special reference to atomic sizes, oxidation states and colour.
Ans: **Atomic sizes:** increase from the first to the second series, but the third series is nearly the same size as the second due to lanthanoid contraction. **Oxidation states:** the 4d and 5d series show a wider range and, especially, greater stability of higher oxidation states than the 3d series. **Colour:** first-series ions are typically more intensely/simply coloured (due to d-d transitions in largely ionic, high-spin complexes), while heavier congeners more often form low-spin complexes and metal-metal bonded clusters, giving somewhat different colour behaviour and a greater tendency towards covalency.

4.36 Illustrate with two examples for each of the following: (i) a transition metal in a low oxidation state stabilised by soft ligands like CO. (ii) a transition metal in a high oxidation state stabilised by hard, small, highly electronegative ligands like O and F.
Ans: (i) Zero (very low) oxidation states are stabilised by carbon monoxide via back-bonding, e.g. **$[Ni(CO)_4]$** (Ni in 0 state) and **$[Fe(CO)_5]$** (Fe in 0 state). (ii) High oxidation states are best stabilised by small, highly electronegative O/F ligands capable of pπ–dπ bonding, e.g. **MnO_4^-** (Mn in +7) and **CrF_6**/**OsO_4** (Cr in +6, Os in +8).

4.37 What is meant by the term "interstitial compound"? Why are such compounds well known for transition metals?
Ans: **Interstitial compounds** are formed when small atoms — hydrogen, carbon, nitrogen or boron — occupy the empty interstitial spaces (voids) within the crystal lattice of a metal, without disturbing its basic

metallic structure. They are well known for transition metals because these metals typically adopt close-packed crystal structures whose octahedral/tetrahedral voids are just the right size to accommodate such small atoms. The resulting compounds retain metallic conductivity and lustre but are typically **harder, denser, and chemically more inert** than the pure metal (e.g. steel and other iron-carbon interstitials, TiC, Fe_3N).

4.38 How is the variability in oxidation states of the transition metals different from that of the non-transition metals? Justify with two examples each.
Ans: Transition metals show oxidation states differing by **units of 1**, since both (n−1)d and ns electrons of comparable energy can be lost or shared one at a time — e.g. **Fe (+2, +3)** and **Mn (+2, +3, +4, +6, +7)**. Non-transition elements show oxidation states differing by **units of 2**, since their ns electron pair is generally lost or retained together — e.g. **Sn (+2, +4)** and **Tl (+1, +3)**, the lower state in the latter favoured by the inert-pair effect.

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