



Class : 11

2023 - 24

The d and f-Block Elements

Position in the Periodic Table

- The d -orbitals of the penultimate energy level of atoms receive electron giving rise to four rows of the transition metals, i.e., $3d$, $4d$, $5d$ and $6d$.

Electronic Configurations of the d-Block Elements

- In general the electronic configuration of outer orbitals of these elements is $(n-1)d^{1-10} ns^{1-2}$.
- Exceptions because of very little energy difference between $(n-1)d$ and ns orbitals. Furthermore, half and completely filled sets of orbitals are relatively more stable.
- A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the $3d$ series. For example, consider the case of Cr, which has $3d^4 4s^2$ configuration instead of $3d^5 4s^1$.
- The electronic configurations of outer orbitals of Zn, Cd, Hg and Cu are represented by the general formula $(n-1)d^{10} ns^2$.
- The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour.

General Properties of the Transition Elements (d-Block)

Physical Properties:

- Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre. With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.
- The transition metals (with the exception of Zn, Cd and Hg) are very hard and have low volatility. Their melting and boiling points are high.
- The high melting points of these metals are attributed to the involvement of greater number of electrons from $(n-1)d$ in addition to the ns electrons in the interatomic metallic bonding.
- Metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series.

Variation in Atomic and Ionic Sizes of Transition Metals :

- In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number. This is because the new electron enters a d -orbital each time the nuclear charge increases by unity.
- Increase from the first ($3d$) to the second ($4d$) series of the elements but the radii of the third ($5d$) series are virtually the same as those of the corresponding members of the second series.
- The filling of $4f$ before $5d$ orbital results in a regular decrease in atomic radii called Lanthanoid contraction. The imperfect shielding of one electron by another in the same set of orbitals. However, the shielding of one f electron by another is less than that of one d electron by another, and as the nuclear charge increases along the series, there is fairly regular decrease in the size of the entire $4f^n$ orbitals.
- The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements.



Ionisation Enthalpies :

- There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner d orbitals.
- The three terms responsible for the value of ionisation enthalpy are attraction of each electron towards nucleus, repulsion between the electrons and the exchange energy. Exchange energy is responsible for the stabilisation of energy state.
- The loss of exchange energy increases the stability. As the stability increases, the ionisation becomes more difficult.
- Mn^+ has $3d^5 4s^1$ configuration and configuration of Cr^+ is d^5 , therefore, ionisation enthalpy of Mn^+ is lower than Cr^+ , In the same way, Fe^{2+} has d^6 configuration and Mn^{2+} has $3d^5$ configuration. Hence, ionisation enthalpy of Fe^{2+} is lower than the Mn^{2+} .

Oxidation States :

- One of the notable features of a transition elements is the great variety of oxidation states these may show in their compounds.
- The elements which give the greatest number of oxidation mates so be in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7 .
- The maximum oxidation states of reasonable stability correspond in mile to the sum of the s and d electrons upto manganese ($Ti^{IV}O_2$, $V^{IV}O_2$, $Cr^{VI}O_4^{2-}$, $Mn^{VII}O_4^-$) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe^{III} , Co^{III} , Ni^{II} , Cu^{II} , Zn^{II} .
- The variability of oxidation states, a characteristic of transition elements arises out of incomplete filling of d orbitals in such a way that the oxidation states differ from each other by unity.
- Low oxidation states are found when a complex compound has ligands capable of π -acceptor character in addition to the σ -bonding. For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

Trends in the M^{2+}/M Standard Electrode Potentials :

Table: Thermochemical data (kJ mol^{-1}) for the first row Transition Elements and the Standard Electrode Potentials for the Reduction of M^{II} to M .

Element (M)	$\Delta_2 H^\circ(M)$	$\Delta_1 H_1^\circ$	$\Delta_1 H_2^\circ$	$\Delta_{\text{hyd}} H^\circ(M^{2+})$	$E^\circ N$
Ti	469	656	1309	-1866	-1.63
V	515	650	1414	-1895	-1.18
Cr	398	653	1592	-1925	-0.90
Mn	279	717	1509	-1862	-1.18
Fe	418	762	1561	-1998	-0.44
Co	427	758	1644	-2079	-0.28
Ni	431	736	1752	-2121	-0.25
Cu	339	745	1958	-2121	-0.34
Zn	130	906	1734	-2059	-0.76



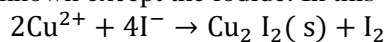
- The unique behaviour of Cu, having a positive E° , accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and bol concentrated sulphuric) react with Cu, the acids being reduced. The high energy to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy.

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials:

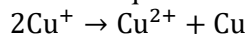
- The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+} . The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas comparatively low value for Fe shows the extra stability of $Fe^{3+}(d^5)$. The comparatively low value for V is related ω the stability of V^{2+} .

Trends in Stability of Higher Oxidation States :

- The highest oxidation numbers are achieved in TiX_4 (tetrahalides). VF_5 and CrF_6 . The +7 state for Mn is not represented in simple halides but $MnO_3 F$ is known, and beyond Mn no metal has a trihalide except FeX_3 and CoF_3 . The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in the case of CoF_3 , or higher bond enthalpy terms for the higher covalent compounds, e.g., VF_5 and CrF_6 .
- Fluorides is their instability in the low oxidation states e.g., $VX_2(X = Cl, Br \text{ or } I)$ and the same applies to CuX . On the other hand, all CuII halides are known except the iodide. In this case, Cu^{2+} oxidises I^- to I_2 :



However, many copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

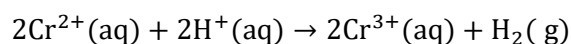


The stability of $Cu^{2+}(aq)$ rather than $Cu^+(aq)$ is due to the much more negative $\Delta_{hyd} H^\circ$ of $Cu^{2+}(aq)$ than Cu^+ , which more than compensates for the second ionisation enthalpy of Cu.

- The highest oxidation number in the oxides coincides with the group number and is attained in Sc_2O_3 to Mn_2O_7 .
- Oxidations stabilise V^V as VO_2^+ , V^{IV} as VO^{2+} and Ti^{IV} as TiO^{2+} . The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine. Thus the highest Mn fluoride is MnF_4 whereas the highest oxide is Mn_2O_7 .

Chemical Reactivity and E° Values :

- Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble' - that is, they are unaffected by single acids. The metals of the first series with the exception of copper are relatively more reactive and are oxidised by $1M H^+$.
- E^\ominus values for Mn, Ni and Zn are more negative than expected from the general trend. Whereas the stabilities of half-filled d subshell (d^5) in Mn^{2+} and completely filled d subshell (d^{10}) in zine are related to their E^e values; for nickel, E^0 value is related to the highest negative enthalpy of hydration. Mn^{3+} and Co^{3+} ions are the strongest oxidising agents in aqueous solutions. The ions Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents and will liberate hydrogen from a dilute acid, e.g.



Formation of Coloured Ions :

- When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed (Unit 9). This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

Formation of Complex Compounds :

- Complex compounds are those in which the metal ions bind a number of anions of neutral molecules giving complex species with characteristic properties.
- The transition metals form a large number of complex compounds. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of d orbitals for bond formation.

Catalytic Properties :

- The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes.



- Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst.
- This has the effect of increasing the concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules (the activation energy is lowering). Also because the transition metal ions can change their oxidation states, they become more effective-as catalysts.

Formation of Interstitial Compounds :

- Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn₄ N, Fe₃H, VH_{0.56} and TiH_{L-7+} etc.
- The principal physical and chemical characteristics of these compounds are as follows:
- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity.
- They are chemically inert.

Alloy Formation :

- An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.
- Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys: chromium, vanadium, tungsten, molybdenum and manganese are used for the production of a variety of steels and stainless steel.

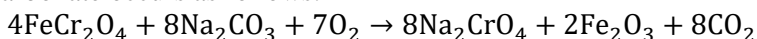
Some Important Compounds of Transition Elements

Oxides and Oxoanions of Metals:

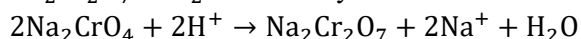
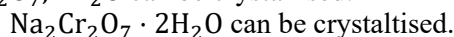
- These oxides are generally formed by the reaction of metals with oxygen at high temperatures. All the metals except scandium form MO oxides which are ionic.
- The highest oxidation number in the oxides, coincides with the group number and is attained in Se₂O₃ to Mn₂O₇.
- As the oxidation number of a metal increases, ionic character decreases.
- Mn₂O₇ gives HMnO₄ and CrO₃ gives H₂CrO₄ and H₂Cr₂O₇, V₂O₅ is, however, amphoteric though mainly acidic and it gives VO₄³⁻ as well as VO₂⁺ salts. In vanadium there is gradual change from the basic V₂O₃ to less basic V₂O₄ and to amphoteric V₂O₅. V₂O₄ dissolves in acids to give VO₂⁺ salts. Similarly, V₂O₅ reacts with alkalis as well as acids to give VO₄³⁻ and 4VO₄⁺ respectively.

Potassium dichromate K₂Cr₂O₇

- Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore (FeCr₂O₄) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:



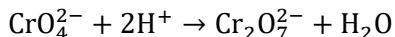
- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, Na₂Cr₂O₇ · 2H₂O can be crystallised.



- Sodium dichromate is more soluble than potassium dichromate. Prepared by treating the solution of sodium dichromate with potassium chloride.

- Na₂Cr₂O₇ + 2KCl → K₂Cr₂O₇ + 2NaCl

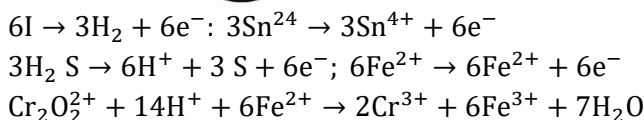
The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution.



- Cr₂O₇²⁺ + 2OH⁻ → 2CrO₄²⁻ + H₂O

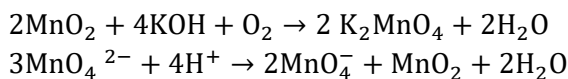
- The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr – O – Cr bond angle of 126°. Sodium and potassium dichromates are strong oxidising agents; Cr₂O₇²⁺ + 14H⁺ + 6e⁻ → 2Cr³⁺ + 7H₂O (E⁻ = 1.33 V)

Acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

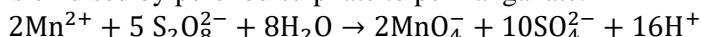


Potassium permanganate $KMnO_4$:

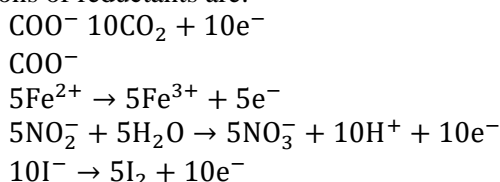
- Potassium permanganate is prepared by fusion of MnO_2 , with an alkali metal hydroxide and an oxidising agent like KNO_3 . This produces the dark green K_2MnO_4 which disproportionates in a neutral or acidic solution to give permanganate.



A manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

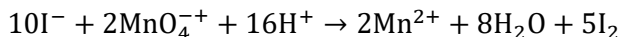


- Potassium permanganate forms dark purple (almost black) crystals which are isostructural with those of $KClO_4$. The salt is not very soluble in water (6.4 g/100 g of water at 293 K), but when heated it decomposes at 513 K.
$$2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$$
- The manganate and permanganate ions are tetrahedral; the π -bonding takes place by overlap of p orbitals of oxygen with d orbitals of manganese. The green manganate is paramagnetic because of one unpaired electron but the permanganate is diamagnetic due to the absence of unpaired electron.
- Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The halfreactions of reductants are:

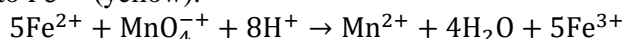


In acid solutions:

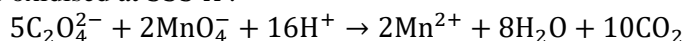
- Iodine is liberated from potassium iodide :



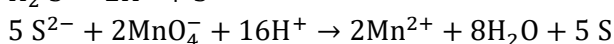
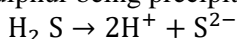
- Fe^{2+} ion (green) is converted to Fe^{3+} (yellow):



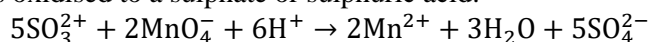
- Oxalate ion or oxalic acid is oxidised at 333 K :



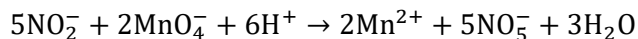
- Hydrogen sulphide is oxidised, sulphur being precipitated.



- Sulphurous acid or sulphite is oxidised to a sulphate or sulphuric acid:

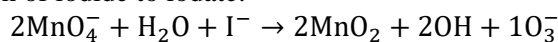


- Nitrite is oxidised to nitrate:

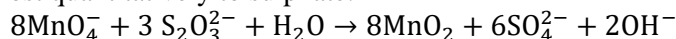


- In neutral or faintly alkaline solutions:

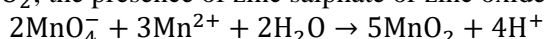
- A notable reaction is the oxidation of iodide to iodate:



- Thiosulphate is oxidised almost quantitatively to sulphate:



- Manganous salt is oxidised to MnO_2 ; the presence of zinc sulphate or zinc oxide catalyses the oxidation:



The Inner Transition Elements (f – Block) :

The f -block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

The Lanthanoids

Atomic and Ionic Sizes :

- The overall decrease in atomic and ionic radii from lanthanum to lutetium (the lanthanoid contraction) is a unique feature in the chemistry of the lanthanoids.



- The decrease in atomic radii (derived from the structures of metals) is not quite regular as it is regular in M^{1+} ions. This contraction is, of course, similar to that observed in an ordinary transition series and is attributed to the same cause, the imperfect shielding of one electron by another in the same sub-shell.
- However, the shielding of one $4f$ electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is fairly regular decrease in the sizes with increasing atomic number.
- The almost identical radii of Zr(160pm) and Hf(159pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

Oxidation States :

- In the lanthanoids, La(II) and Ln(III) compounds are predominant species. However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.
- This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshell. The formation of Ce^N is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.
- The E° value for Ce^{4+}/Ce^{3+} is +1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence $Ce(IV)$ is a good analytical reagent.

Table : Electronic Configurations and Radii of Lanthanum and Lanthanoids

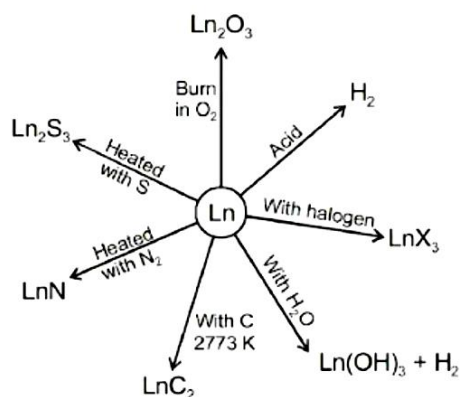
Atomic Number	Name	Symbo	Electronic configurations			Radii/pm		
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	ln	Ln^3
57	Lanthanum	La	$5d^1 6s^2$	$5d'$	$4f^\circ$		18	10
58	Cerium	Ce						
58	Cerium	Pr	4 $/5d^3 6s^2$	$4f^2$	$4f'$	$4f^\circ$	18	10
59	Praseodymium		$4f^3 6s^2$	$4f^3$				
60	Neodymium	Nd	$4f^4 6s^2$	$4f^3$ $4f^4$	$4f^2$	$4f'$	18	10
61	Promethium	Pm	$4f^5 6s^2$	$4f^n$ $4f^5$	$4f^3$	$4f^2$	18	99
62	Samarium	Sm	$4f^6 6s^2$	$4f^6$	$4f^4$ $4f^5$		18	98
63	Europium	Eu	$4f^7 6s^2$	$4f^7$	$4f^3$ $4f^6$		18	96
64	Gadolinium	Gd	$4f^3 5d^1 6s^2$	$4f^3 5d^1$	$4f'$ $4f^7$		19	95



65	Terbium	Tb	$4f^6 6s^2$	$4f^9$	$4f^8$	$4f^7$	18	94
66	Dysprosium	Dy	$4f^{10} 6s^2$	$4f^{10}$	$4f^9$		17	92
67	Holmium	Ho	$4f^{11} 6s^2$	$4f^{11}$	$4f^{10}$	$4f^8$	17	91
68	Erbium	Er	$4f^{12} 6s^2$	$4f^{12}$	$4f^{11}$		17	89
69	Thulium	Tm	$4f^{13} 6s^2$	$4f^{13}$	$4f^{12}$		17	88
70	Ytterbium	Yb	$4f^{14} 6s^2$	$4f^{14}$	$4f^{13}$		17	87
71	Lutetium	Lu	$4f^{14} 5d^1 6s^2$	$4f^{14} 5d^1$	$4f^{14}$	-	17	86

General Characteristics

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air. The hardness increases with increasing atomic number.
- They have typical metallic structure and are good conductors of heat and electricity. Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.
- Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions, Colour of these ions may be attributed to the presence of f electrons.
- Fig : Chemical reactions of the lanthanoids.



- A well known alloy is mischmetal which consists of a lanthanoid metal (95%) and iron (5%) and traces of S, C, Ca and Al. A good deal of mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint. The Actinoids The actinoids include the fourteen elements from Th to Lr.

The Actinoids

The actinoids include the fourteen elements from Th to Lr.

Table : Some Properties of Actinium and Actinoids



Atomic Number	Name	Symbol	Electronic configurations			Radii/pm	
			M	M ³⁺	M ¹⁺	M ³⁺	M ⁴⁺
89	Actinium	Ac	$6d^1 7s^2$	$5f^0$		111	
90	Thorium	Th	$6d^2 7s^2$	$5f'$	$5f^0$		99
91	Protactinium	Pa	$5f^2 6d^2 7s^2$	$5f^2$	$5f'$		96
92	Uranium	U	$5f^3 6d^2 7s^2$	$5f'$	$5f^2$	103	93
93	Neptunium	Np	$5f^4 6d^1 7s^2$	$5f^4$	$5f^3$	101	92
94	Plutonium	Pu	$5f^4 7s^2$	$5f^5$	$5f^4$	100	90
95	Americium	Am	$5f^6 7s^2$	$5f^6$	$5f^5$	99	89
96	Curium	Cm	$5f^7 7s^2$	$5f^7$	$5f^0$	99	88
97	Berkelium	Bk	$5f^7 6d^1 7s^2$	$5f^8$	$5f^7$	98	87
98	Californium	Cf	$5f^8 7s^2$	$5f^9$	$5f^8$	98	89
99	Einsteinium	Es	$5f^{11} 7s^2$	$5f^{10}$	$5f^9$	-	=
100	Fermium	Fm	$5f^{12} 7s^2$	$5f^{11}$	$5f^{16}$	-	-
101	Mendelevium	Md	$5f^3 7s^2$	$5f^{12}$	$5f^{11}$	-	-
102	Noblium	No	$5f^{14} 7s^2$	$5f^{13}$	$5f^{12}$	-	-
103	Lawrencium	Lr	$5f^{14} 6d^1 7s^2$	$5f^{14}$	$5f^{13}$	-	-

The actinoids are radioactive elements.

Electronic Configurations :

- All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the $5f$ and $6d$ subshells.
- Ionic Sizes :** There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by $5f$ electrons.

Oxidation States :

- There is a greater range of oxidation states, $5f$, $6d$ and $7s$ levels are of comparable energies.
- The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states.

General Characteristics and Comparison with Lanthanoids

- The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids. The actinoids are highly reactive metals.
- The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired $5f$ electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values.
- The ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when $5f$ orbitals are beginning to be occupied,



they will penetrate less into the inner core of electrons. The $5f$ electrons, will therefore, be more effectively shielded from the nuclear charge than the $4f$ electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

Some Applications of d-and f-Block Elements

- Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells.
- Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid. TiCl_4 with $\text{Al}(\text{CH}_3)_3$ forms the basis of the Ziegler catalysts used to manufacture polyethylene (polythene).
- In the Wacker process the oxidation of ethyne to ethanal is catalysed by PdCl_2 .



PW Web/App - <https://smart.link/7wwosivoicgd4>

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