

Descriptive Chemistry of Elements

***d*-Block**

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1. Introduction to *d*-block elements

Introduction

These lessons deal with the chemistry of *d*-block elements. The chemistry of *d*-block elements is very interesting and varies significantly from the chemistry of *s*- and *p*-block elements. This lesson introduces important concepts and terms such as electron configurations of metal centres, composition of coordination compounds, oxidation number, coordination number and geometries of coordination compounds that are needed to understand subsequent lessons.

1.1 *d*-Block

The filling of electrons into the *d*-levels creates the ***d*-block**. In a free metal, the *nd*-electrons fill after the filling of (n+1)*s*-electrons and before the filling of (n+1)*p*-electrons, thus, the *d*-block elements are situated between those of *s*- and *p*-block elements. Generally, the electron configuration of a *d*-block element can be represented as (n+1)*s*² *nd*^m or (n+1)*s*¹ *nd*^m where n = 3, 4, 5 or 6 and m = 1, 2, 3,or 10.

When you look at the Periodic Table, you can see, that there are **four series** (or rows) in the *d*-block. They are the *3d*, *4d*, *5d* and *6d*-series and are in the 4th, 5th, 6th and 7th periods, respectively.

The elements in the *3d*-series (Z = 21 to 30)

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30

The elements in the *4d*-series (Z = 39 to 48)

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48

The elements in the *5d*-series (Z = 57, 72 to 80)

Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80

The elements in the 6d-series (Z = 89, 104 to 112)

Element	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112

3d-elements and 4d-elements have atomic numbers 21-30 and 39-48, respectively. The elements listed in a vertical column belong to a Group, so that, Sc, Y, La and Ac belong to the **same Group** and it is called Group 3; similarly Cr, Mo and W belong to Group 6 and so on. At the Foundation Level we will concentrate more on the chemistry of 3d-elements.

1.2 3d-Elements

The filling of 3d-orbitals results in 3d-elements. We know that the electron configuration of an atom provides valuable information about the properties of an atom or its compounds. For example, the electron configuration of Ca = $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ and calcium readily forms the Ca^{2+} ion.

We know that the order of filling of energy levels is 1s, 2s, 2p, 3s, 3p, **4s, 3d**, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, etc. There are five 3d-orbitals and each orbital can have a maximum of two electrons. Let us look at the electron configurations of 3d-elements.

1.3 Electron configuration of 3d-elements

Scandium is the first 3d-element and its electron configuration is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$. The electron configurations and Group numbers of 3d-elements (Z = 21 to 30) are given below.

Element (Name)	Z	E ⁿ configuration	Group no.
Sc (Scandium)	21	[Ar]4s ² 3d ¹	3
Ti (Titanium)	22	[Ar]4s ² 3d ²	4
V (Vanadium)	23	[Ar]4s ² 3d ³	5
Cr (Chromium)	24	[Ar]4s ¹ 3d ⁵	6
Mn (Manganese)	25	[Ar]4s ² 3d ⁵	7
Fe (Iron)	26	[Ar]4s ² 3d ⁶	8
Co (Cobalt)	27	[Ar]4s ² 3d ⁷	9
Ni (Nickel)	28	[Ar]4s ² 3d ⁸	10
Cu (Copper)	29	[Ar]4s ¹ 3d ¹⁰	11
Zn (Zinc)	30	[Ar]4s ² 3d ¹⁰	12

Note that [Ar] = $1s^2 2s^2 2p^6 3s^2 3p^6$ and also the electron configurations of Cr and Cu are [Ar]4s¹3d⁵ and [Ar]4s¹3d¹⁰, respectively.

Group number

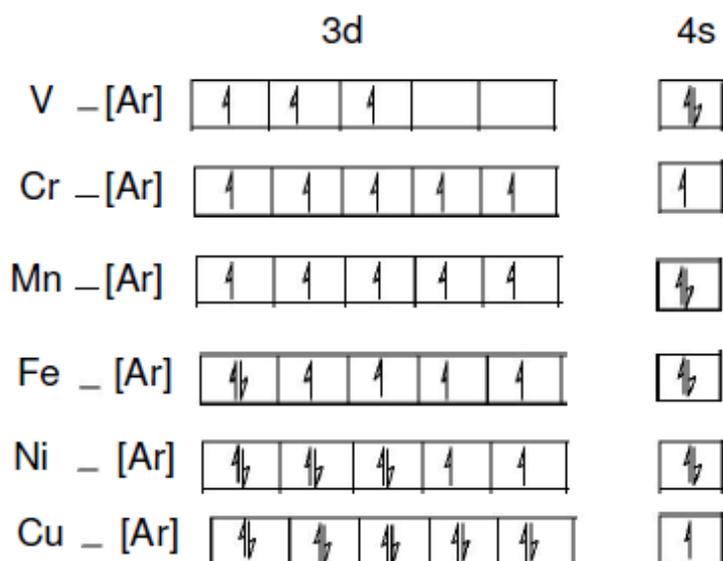
The Group number is equal to the sum of 4s and 3d electrons in the *free metal* (i.e. zerovalent metal or M^0). For example, the electron configuration of Sc is $[\text{Ar}]4s^23d^1$ or $[\text{Ar}]3d^14s^2$, thus the Group number of Sc is 3. Therefore, the elements Sc, Y and La belong to **Group 3** (formerly Group IIIB); the elements Fe, Ru, Os belong to **Group 8** (formerly Group VIII B) and the elements Zn, Cd, and Hg belong to **Group 12** (formerly Group IIB).



Activity

1. Molybdenum (Mo) is a Group 6 metal in the 5th period. Write the electron configuration of it.
2. What is the electron configuration of the element with the atomic number 40?

There are five 3d-orbitals and one 4s-orbital. The electron configurations of 3d-elements can also be represented as shown below where the distribution of valence electrons in the five 3d-orbitals and the 4s orbital are indicated; each square represents an orbital. The electron configurations of V, Cr, Mn, Fe, Ni and Cu are given below.



You can see that all these elements have **unpaired electrons** (e.g. V and Cr have 3 and 6 unpaired electrons, respectively), thus, they are **paramagnetic**.

Q : Why do we write electron configurations of Cr and Cu as $[\text{Ar}]3d^54s^1$ and $[\text{Ar}]3d^{10}4s^1$?

A : There are five *d*-orbitals. The reason for this is that the *exactly half-filled* (i.e. d^5) and *completely filled* (i.e. d^{10}) *d*-orbitals possess **extra stability**.

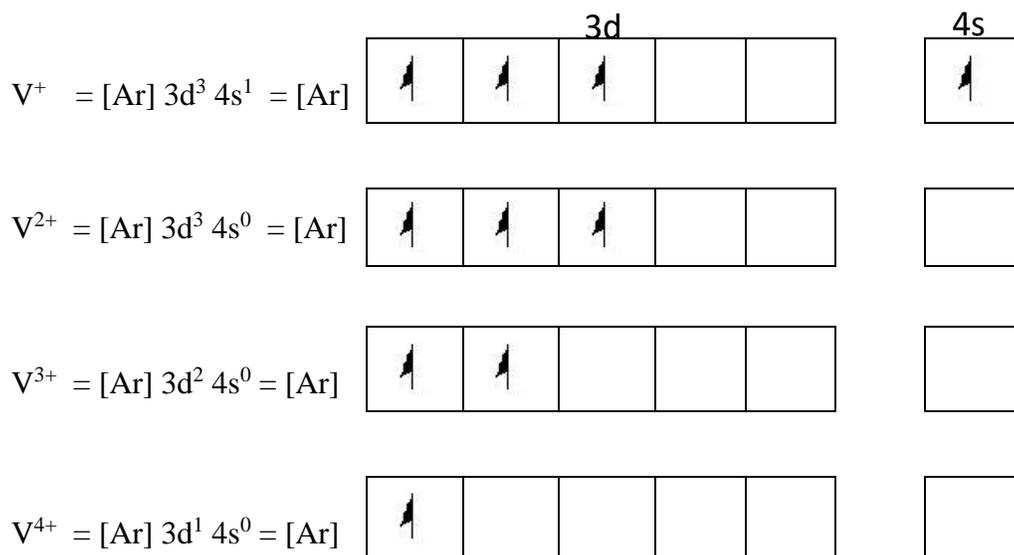


Activity

3. Give the electron distribution of the valence electrons in the five *3d*-orbitals and the *4s* orbital of zerovalent cobalt. Determine the number of unpaired electrons in it.

1.4 Electron configuration of cations

Removal of an electron(s) from a zerovalent metal (M^0) generates a **cation**. For example, V^+ , V^{2+} , V^{3+} and V^{4+} can be formed, by removing 1, 2, 3 and 4 electron(s) respectively from V^0 . The electron configurations of V^+ , V^{2+} , V^{3+} and V^{4+} ions are given below.



Note that the *4s*-electrons were removed before the removal of the *3d*-electrons. The reason for this is that in a **metal cation** the energy of *3d*-orbitals is lower than the energy of *4s*-orbitals (c.f. when filling electrons, the energy of the *4s* orbital is lower than *3d*-orbitals). Thus the valence electron configuration of V^+ can be considered as $3d^4$.



Activity

4. Determine the electron configurations of Co^+ and Co^{3+} .

1.5 Transition elements

A transition element (M) should form at least one ion (M^+ , M^{2+} or M^{3+}) with a **partly filled *d*-shell**. Transition metals show variable oxidation states and form coloured complex ions. Cu is a transition metal since it forms Cu^{2+} with the electron configuration $[\text{Ar}]3\text{d}^94\text{s}^0$, Cu also forms coloured compounds. Normally, Sc and Zn are not considered as transition elements as Sc forms only Sc^{3+} with no *d*-electrons (3d^0) whilst Zn forms only Zn^{2+} with a full *d*-sub shell (3d^{10}). In some text books, Sc is considered as a transition metal because Zero valent scandium (Sc^0) has a partly filled *d*-shell, $[\text{Ar}]3\text{d}^14\text{s}^2$ or $[\text{Ar}]4\text{s}^23\text{d}^1$.

1.6 Ligands

A **molecule** or an **ion** with a **donor atom(s)** can act as a *ligand*. Some are neutral (*e.g.* NH_3 , CO, H_2O) and some are negatively charged (Cl^- , CN^- , CO_3^{2-} , SO_4^{2-}).

For example, NH_3 can donate the lone-pair of electrons on N to a metal centre (M^{n+}) to form a **coordinate or dative bond**.



Note that other ligands on M^{n+} are not shown for clarity. In this case, the nitrogen (**N**) is the **donor atom** or the **coordinating atom**.

1.7 Coordination Compounds

Interaction of a *metal centre* or the *central atom* (M) with a number of *ligands* (L) gives a coordination compound as shown below.



The formula of a neutral coordination compound or complex ion is always written within **square brackets** []. When we write the **chemical formula** of a coordination compound, first write the symbol of the metal, then the symbols of the negative ligands followed by the symbols of the neutral ligands. When there are more than one anionic ligand, write them in alphabetical order, so are the neutral ligands. Chemical formulae of some compounds are given below.

1. $[\text{CrBr}_3(\text{NH}_3)_3]$ but **not** $[\text{Cr}(\text{NH}_3)_3\text{Br}_3]$
2. $[\text{FeClF}_2(\text{NH}_3)_3]$ but **not** $[\text{FeF}_2\text{Cl}(\text{NH}_3)_3]$
3. $[\text{CoBr}_3(\text{NH}_3)(\text{CO})_2]$ but **not** $[\text{CoBr}_3(\text{CO})_2(\text{NH}_3)]$

It is important to know that a coordination compound **does not** dissociate into its components when it is dissolved in a solvent.



Activity

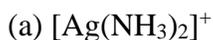
5. Give simple salts and coordination compounds that could be formed in a solution containing Na^+ , Fe^{3+} , CN^- and NH_3 .

1.8 Oxidation Number (O.N.)

The oxidation number of a metal centre is the charge left on the metal when all the ligands are removed. For example, removal of three Br^- ions and three neutral ammonia molecules from $[\text{CoBr}_3(\text{NH}_3)_3]$ leaves three positive charges on cobalt. Therefore, the oxidation number of cobalt in $[\text{CoBr}_3(\text{NH}_3)_3]$ is +3 or +III.

Note that the sum of charges inside the square bracket [] is equal to the charge of the complex ion []ⁿ⁺ or []ⁿ⁻ (written outside the bracket). For a neutral complex like $[\text{CoBr}_3(\text{NH}_3)_3]$, $n = 0$.

Q : Determine the **oxidation number** of each of the following metal centres



A : NH_3 is a *neutral* ligand and the charge on N is *zero*. Cl^- is a *monoanionic* ligand thus the charge on chlorine is -1 . $[\text{Ag}(\text{NH}_3)_2]^+$ is a complex cation and its charge is $+1$. $[\text{NiCl}_2(\text{NH}_3)_2]$ is a neutral complex and its charge is zero.

The oxidation numbers of silver and nickel can be calculated as given below. Let us assume that the **oxidation number** of each metal centre is y . Now determine the sum of **charges** inside the square brackets, which is equal to the charge of the complex/complex ion.

(a) Sum of charges inside [] = $y + 2 \times (0) = +1 = \text{charge of the complex cation}$

$$y = +1 \quad \text{oxidation number of Ag} = +1$$

(b) Sum of charges inside [] = $y + 2 \times (-1) + 2 \times (0) = 0$

$$y = +2 \quad \text{oxidation number of Ni} = +2$$



Activity

6. Determine the oxidation number of iron in $[\text{Fe}(\text{CN})_6]^{4-}$.

1.9 Coordination number (C.N.)

We know that ligands are Lewis bases and donate electron pairs to vacant d orbitals of the central metal to form coordinate bonds. The number of such directly bonded atoms is referred to as the **coordination number** of the metal.

For example, the coordination number of iron and silver in $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Ag}(\text{NH}_3)_2]^+$ are 6 and 2, respectively.



Activity

7. Determine the coordination numbers of metal centres in $[\text{CrBrCl}_2(\text{NH}_3)_3]$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ and $[\text{Fe}(\text{CO})_5]$.

1.10 Geometry

C.N.	Geometry	(formula)	Example
2	Linear	$[ML_2]$	$NC-\bar{A}g-CN$
3	Trigonal planar	$[ML_3]$	$\left[\begin{array}{c} \text{CN} \\ \diagup \\ \text{NC}-\text{Cu} \\ \diagdown \\ \text{CN} \end{array} \right]^{2-}$
4	Tetrahedral	$[ML_4]$	$\left[\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{Cu} \\ \diagdown \quad \diagup \\ \text{Cl} \quad \text{Cl} \end{array} \right]^{2-}$
4	Square planar	$[ML_4]$	$\left[\begin{array}{c} \text{H}_3\text{N} \quad \text{NH}_3 \\ \diagdown \quad \diagup \\ \text{Cu} \\ \diagup \quad \diagdown \\ \text{H}_3\text{N} \quad \text{NH}_3 \end{array} \right]^{2+}$
5	Trigonal bipyramidal	$[ML_5]$	$\begin{array}{c} \text{CO} \\ \\ \text{OC}-\text{Fe} \cdots \text{CO} \\ \diagdown \quad \diagup \\ \text{CO} \quad \text{CO} \\ \\ \text{CO} \end{array}$
5	Square pyramidal	$[ML_5]$	$\left[\begin{array}{c} \text{CN} \\ \\ \text{NC} \cdots \text{Ni} \cdots \text{CN} \\ \diagdown \quad \diagup \\ \text{NC} \quad \text{CN} \end{array} \right]^{3-}$
6	Octahedral	$[ML_6]$	$\left[\begin{array}{c} \text{NH}_3 \\ \\ \text{H}_3\text{N} \cdots \text{Co} \cdots \text{NH}_3 \\ \diagdown \quad \diagup \\ \text{H}_3\text{N} \quad \text{NH}_3 \\ \\ \text{NH}_3 \end{array} \right]^{3+}$

Table 1: Variation of geometry with the coordination number of the metal

The spatial arrangement of ligands (L) around the central metal (M) defines the geometry (or the shape) of the complex. The geometry varies with the coordination number of the metal as given in Table 1. For example, a compound with the formula $[\text{ML}_2]$ has the linear geometry; a compound with the formula $[\text{ML}_4]$ can show two different types of geometry – **tetrahedral** and **square-planar**; a compound with the formula $[\text{ML}_5]$ can show two different types of geometry – trigonal bipyramidal and square-pyramidal.



Activity

8. What are the geometries of (i) CO_3^{2-} , (ii) MnO_4^- and (iii) I_3^- ?

Summary

- The filling of electrons into the *d*-levels creates the ***d*-block**. The *3d*, *4d*, *5d* and *6d*-series are in the 4th, 5th, 6th and 7th periods, respectively.
- Generally, the electron configuration of a *d*-block element can be represented as $(n+1)s^2nd^m$ or $(n+1)s^1nd^m$ where $n = 3, 4, 5$ or 6 and $m = 1, 2, 3, \dots$ or 10 . The elements from Sc to Cu have unpaired electrons, thus, they are **paramagnetic**.
- The Group number is equal to the sum of *4s* and *3d* electrons in the free metal.
- A transition element is the one, which has at least one ion with a partly filled *d*-shell. On the chemical behaviour, Sc and Zn are not considered as transition elements.
- A molecule or an ion with a donor atom(s) can act as a ligand. Some are neutral (*e.g.* NH_3 , CO , H_2O) and some are negatively charged (*e.g.* Cl^- , CN^- , CO_3^{2-} , SO_4^{2-}).
- The oxidation number of a metal centre is the charge left on the metal when all the ligands are removed.
- The number of such directly bonded atoms is referred to as the coordination number of the metal.



Learning Outcomes

Once you have finished studying this lesson you should be able to

- determine the Group number of a *d*-element.
- identify neutral, anionic ligands, simple salts and coordination compounds.
- write the electron configuration of 3*d*-elements and their cations.
- calculate the oxidation number of a metal center.
- determine the coordination number of a metal center.
- suggest the geometry of a simple coordination compound or a complex ion.



Activity

9. Determine the oxidation and coordination numbers of each of the metal centres of the following complexes.
- $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]\text{SO}_4$
 - $[\text{CoCl}(\text{CN})(\text{NO}_2)(\text{NH}_3)_3]$
 - $[\text{CoCl}(\text{NH}_3)_5](\text{NO}_3)_2$
 - $\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$
10. Draw the structures of the following compounds/complex ions.
- $[\text{Ag}(\text{NH}_3)_2]^+$
 - $[\text{Ni}(\text{CO})_4]$
 - $[\text{Ni}(\text{CN})_4]^{2-}$
 - $[\text{Fe}(\text{CO})_5]$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$
11. Write the electron configurations of Cu^{2+} , Fe^{3+} and Mn^{2+} . Give the formula of a compound or ion containing manganese in an oxidation state of +7.
12. Identify the shapes of the following molecules.
- (i) HCl (ii) BF_3 (iii) CH_4 (iv) PCl_5

2. Properties of *d*-block elements

Introduction

In this lesson, we will look at the properties of *d*-block elements such as conductivity, melting and boiling points, electronegativity, ionization energy, ionic radii, variable oxidation states and catalytic properties of metal complexes. Here we will mainly consider the properties of *3d*-elements. *d*-Block elements play important roles as an oxygen carrier in blood (haem unit), active sites in enzymes, medicine (cisplatin), vitamin B₁₂, and catalysts in industrial processes. One important aspect of *d*-elements is that their ability to form various labile complexes with inorganic and organic molecules/ions.

2.1 Metallic character and conductivity

All *3d*-elements are metals. Each consists of a *positively charged lattice* and a *pool of free electrons*. All *3d*-elements are good heat and electrical conductors. The electrical conductivity is facilitated by the presence of free electrons. The metal lattice helps disperse heat energy rapidly.

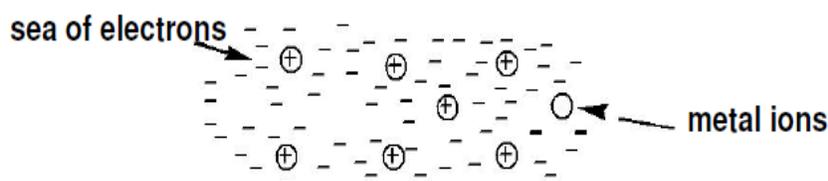


Figure 1: Model of a metal

2.2 Melting and boiling points

d-Block elements have higher melting and boiling points than *s*-block elements. Some properties of *3d*-elements are given in Table 2. In the *3d*-series, the melting point gradually increases from Sc to V and then decreases from Fe to Zn (see Figure 2). Mn has lower melting and boiling points than those of Cr and Fe. Zn has the lowest melting and boiling points compared to other elements in the *3d*-series (Figure 2).

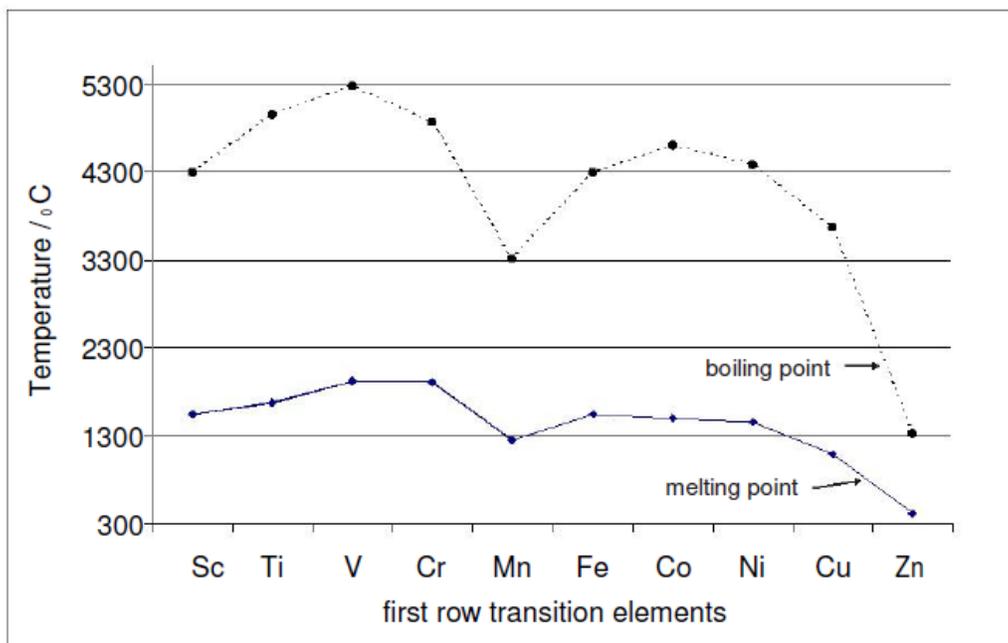


Figure 2: Melting and boiling points of elements from Sc to Zn

2.3 Density and Electronegativity

d-Block elements show higher densities compared to *s*- and *p*-block elements. In the 3*d*-series, the density increases from Sc to Cu (see Figure 3). The densest elements are Os and Ir with a value of 22.6 g cm⁻³. *d*-Block elements are less electropositive than the Group 1 metals. In the 3*d*-series, the electronegativity tends to increase slightly from Sc to Cu (Figure 4).

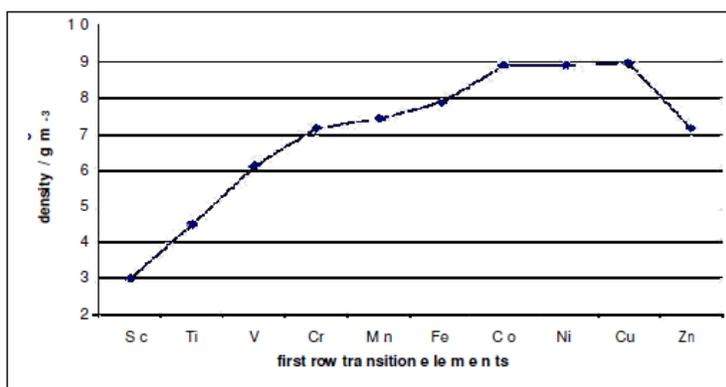


Figure 3: Variation of density in the 3*d*-series

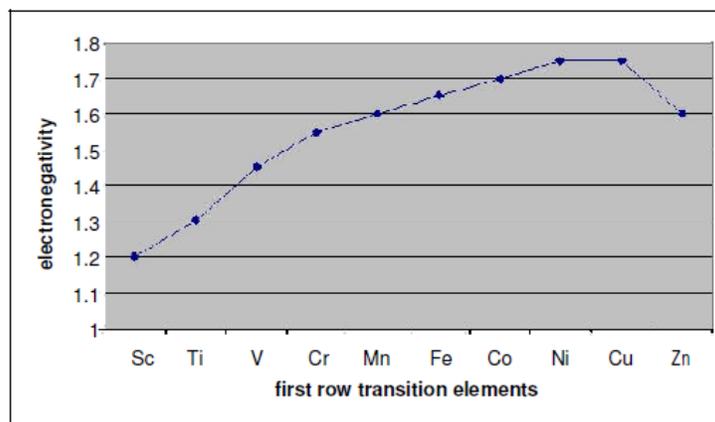


Figure 4: Variation of electronegativity in the 3d-series

Table 2: Some properties of 3d-elements

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radius/pm	144	132	122	118	117	117	116	115	117	125
Ionic radius (M^{2+})/pm	-	86	79	80	83	78	75	69	73	74
Melting point/ °C	1539	1667	1915	1900	1244	1535	1495	1452	1083	420
Boiling point/ °C	2748	3285	3350	2960	2060	2750	3100	2920	2570	907
Density/ (g cm⁻³)	3.01	4.51	6.11	7.14	7.43	7.86	8.90	8.91	8.96	7.14
Electronegativity	1.2	1.3	1.45	1.55	1.6	1.65	1.7	1.75	1.75	1.6
$E^0 (M^{2+}/M) / V$	-	-1.63	-1.17	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76

2.4 Ionic radii

We expected atomic and ionic radii to decrease from Sc to Zn. However, the experimental values obtained for ionic radii of M^{2+} ions showed a curve with two minimums for V and Ni. In other words, the ionic radii of M^{2+} ions gradually decrease from Sc to V and then increase from V to Mn. A similar pattern is observed from Mn to Zn with a minimum for Ni. In the 3d-series, Ni shows the minimum ionic radius for the divalent ion (see Table 2 and Figure 5).

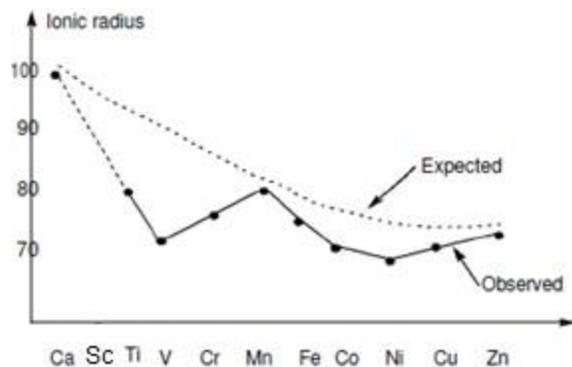


Figure 5: Variation of ionic radii of M^{2+} ions in the 3d-series

2.5 Ionization energy

The first ionization energy of the 3d-elements tends to increase slightly from Sc to Zn (see Table 3). (see Table 3). The 4th ionization energy of Sc is significantly higher than the 3rd ionization energy as the 4th electron has to be removed from an inner orbital (3p) having lower energy. Similarly, the 5th ionization energy of Ti is significantly higher than its 4th ionization energy.

Table 3: Ionization energies of 3d-elements

Elements	Ionization Energy / kJ mol ⁻¹					
	1 st	2 nd	3 rd	4 th	5 th	6 th
Sc	632	1235	2390	7130	8870	10700
Ti	655	1310	2650	4170	9620	11600
V	650	1415	2830	4600	6280	12400
Cr	653	1590	2990	4900	7070	8700
Mn	716	1510	3250	5190	7360	9750
Fe	762	1560	2960	5400	7620	10100
Co	757	1640	3230	5100	7910	10500
Ni	736	1750	3395	5400	7620	10900
Cu	745	1960	3550	5690	7990	10500
Zn	908	1730	3828	5960	8280	11000

2.6 Variable oxidation states

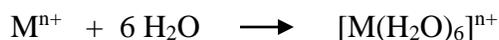
3d-Elements except Sc and Zn show variable oxidation states as shown in Table 4. The most common oxidation states are in **bold** numbers. Mn shows the oxidation number +7. The highest oxidation number shown by a *d*-block element is +8, for example Ru⁸⁺ and Os⁸⁺.

Table 4: Possible oxidation numbers of 3d-elements

Elements	Oxidation number										
	-2	-1	0	+1	+2	+3	+4	+5	+6	+7	+8
Sc					(+2)	+3					
Ti		(-1)	(0)		+2	+3	+4				
V		(-1)	(0)	(+1)	+2	+3	+4	+5			
Cr			(0)	(+1)	+2	+3	(+4)	(+5)	+6		
Mn		(-1)	(0)	(+1)	+2	+3	+4	(+5)	+6	+7	
Fe	(-2)		(0)	(+1)	+2	+3	(+4)	(+5)	(+6)		
Co		(-1)	(0)	(+1)	+2	+3	(+4)				
Ni			(0)	(+1)	+2	(+3)	+4				
Cu				+1	+2	(+3)					
Zn					+2						

2.7 Colours of aqua-complexes

Most of the compounds of transition metal centres are coloured. Metal ions dissolve in water to give aqua-complexes of the type $[M(H_2O)_6]^{n+} = M^{n+}(aq)$.



The colours of some aqua-complexes, *i.e.* $[M(H_2O)_6]^{n+}$, are given in next page.

Metal Centre (aqueous medium)	Colour
Sc³⁺	Colourless
Ti³⁺	Violet
V²⁺	Violet/ Mauve
V³⁺	Violet/ Green
Cr²⁺	Blue
Cr³⁺	Green/ Violet
Mn²⁺	Pale pink
Mn³⁺	Violet or Red
Fe²⁺	Pale green
Fe³⁺	Yellow/ Brown
Co²⁺	Pale pink
Co³⁺	Blue
Ni²⁺	Green
Cu²⁺	Blue
Zn²⁺	Colourless

2.8 Catalysts

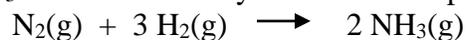
Transition metal complexes play an important role as catalysts. *A catalyst is a substance that increases the rate of a reaction and it is regenerated at the end of the conversion.* A catalyst offers the reactants an alternative, low-energy pathway to products. In other words it lowers the activation energy barrier.

There are two types of catalysts.

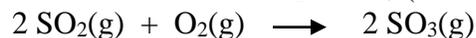
- (i) Homogeneous catalysts (they are present in the same phase as the reagents) and
- (ii) Heterogeneous catalysts (they are present in a different phase to that of the reagents, for example, insoluble solid catalyst in a solution).

Some catalytic reactions are given below. Heterogeneous catalysts are used in reactions 1 to 7.

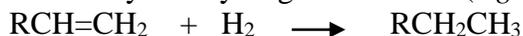
1. Iron or Fe_2O_3 is used as a catalyst in the Haber process of NH_3 synthesis.



2. V_2O_5 catalyses the oxidation of SO_2 to SO_3 (Contact process of H_2SO_4 synthesis).



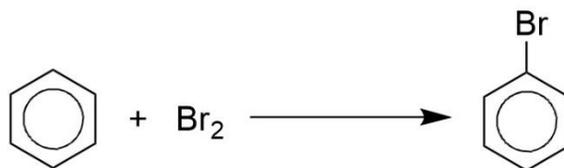
3. Ni is used as a catalyst to hydrogenate olefins (*e.g.* manufacture of margarine).



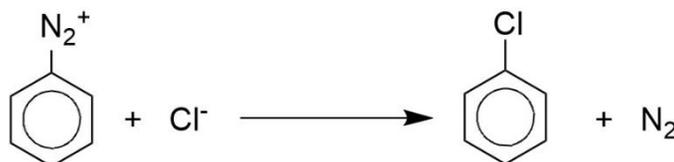
4. Ziegler-Natta catalyst (TiCl_3 and AlEt_3) is used to polymerize olefins (*e.g.* ethylene to polyethylene).



5. Ferric bromide catalyzes the bromination of benzene (Friedel-Crafts reaction).



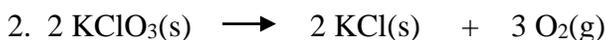
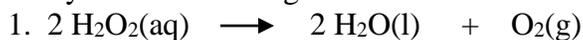
6. CuCl is used in the preparation of chlorobenzene from the corresponding diazonium salt (Sandmeyer reaction).



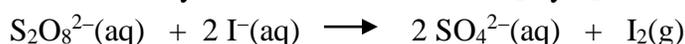
7. Pt-Rh alloy catalyses the oxidation of NH_3 to NO (Ostwald process of HNO_3 synthesis).



8. MnO_2 catalyses the following reactions.



9. Ferrous ions catalyze the oxidation of I^- to I_2 by $\text{S}_2\text{O}_8^{2-}$



Summary

- All $3d$ -elements are good heat and electrical conductors. The electrical conductivity is facilitated by the presence of free electrons.
- In the $3d$ -series, the melting point gradually increases from Sc to V and then decreases from Fe to Zn.
- In the $3d$ -series, the density increases from Sc to Cu.
- In the $3d$ -series, the electronegativity tends to increase slightly from Sc to Cu.
- The first ionization energy of the $3d$ -elements tends to increase slightly from Sc to Zn.
- $3d$ -Elements except Sc and Zn show variable oxidation states.
- Most of the compounds of transition metal centres are coloured.
- Transition metal complexes play an important role as catalysts. They increase the rate of a reaction and are regenerated at the end of the conversion.



Learning Outcomes

At the end of this lesson you should be able to

- discuss the physical properties of $3d$ -elements such as conductivity, melting and boiling points, electronegativity, ionization energy, ionic radii, variable oxidation states and catalytic properties of metal complexes.
- find out the oxidation state of transition metal centres
- identify the colours of aqua complexes of $3d$ - elements
- discuss the reactions / processes catalyzed by $3d$ -elements



Activity

13. Comment on the variation in melting points in the $3d$ -series.
 14. Compare the densities of $3d$ elements with the densities of s -block elements.
 15. Write the order of increasing electronegativity of the $3d$ -elements.
 16. What is the most common oxidation state of nickel and copper?
 17. What is the highest oxidation state shown by a $3d$ -element?
 18. Which $3d$ -elements form colourless aqua complexes?
 19. Which cations of $3d$ -elements form pink aqua complexes?
 20. What is the catalyst used in the Haber process?
 21. What is the catalyst used for manufacturing of margarine?
-

3. Nomenclature of inorganic compounds

Introduction

In lesson 1, we studied the metal-ligand interactions of coordination compounds and their geometries. We know that in a coordination compound the metal centre is surrounded by a set of ligands and we also know how to determine the coordination and oxidation numbers of a metal centre. It is important to have a systematic method of naming these compounds and complex cations/anions. We should be able to draw the structure of a coordination compound from its name. In this lesson, we will learn the IUPAC rules of naming simple inorganic compounds and also coordination compounds. Let us consider the naming of simple inorganic compounds.

3.1 Simple inorganic compounds

Acids, bases and salts can be considered as simple inorganic compounds. In solutions, they dissociate to give a mixture of simple cations and anions. When naming simple acids, the oxidation number of the non-metal (*e.g.* N, S, C) is given in brackets.

Q: Give the IUPAC names of (a) HNO_3 and (b) HNO_2 . What are the cations and anions formed due to dissociation?

A: (a) Nitric(V) acid and (b) Nitric(III) acid.

Note: the oxidation number of N in HNO_3 is +5 (or V) and that of HNO_2 is +3 (or III).

The cation that would be formed due to dissociation is H^+ , and the respective anions are NO_3^- and NO_2^- .

When naming simple salts: (i) first write the name(s) of cation(s) with the oxidation number of the metal in brackets, (ii) the name of the anion with the oxidation number of the non-metal in brackets.

Q: Give the IUPAC names of (a) FeSO_4 and (b) $\text{Fe}_2(\text{SO}_3)_3$.

A: (a) Iron(II) sulfate(VI) and

(b) Iron(III) sulfate(IV).

Note that the oxidation number of S in FeSO_4 is +6 (or VI) and that of $\text{Fe}_2(\text{SO}_3)_3$ is +4 (or IV).

There is a gap between the names of the cation and the anion. The oxidation number of the cation or the anion is not given when it shows **only one** oxidation state, *e.g.* Na^+ , Al^{3+} , NH_4^+ and F show only one oxidation state.

Q: Give the IUPAC name of (a) NH_4F , (b) NaHCO_3 and (c) $(\text{NH}_4)_2\text{CrO}_4$.

A: (a) Ammonium fluoride and
(b) Sodium hydrogen carbonate(IV) and
(c) Ammonium chromate(VI).

Note that the cations other than hydrogen are listed in alphabetical order.

The name of the anion ends with **ide** or **ate**. For example,

Cl^-	chloride	CO_3^{2-}	carbonate
HO^-	hydroxide	SO_4^{2-}	sulfate/sulphate
N^{3-}	nitride	CrO_4^{2-}	chromate



Activity

22. Give the IUPAC names of the following simple inorganic compounds.

- | | | | |
|--------------------------|------------------------------|---------------------------------------|----------------------|
| (a) HClO | (b) HClO_3 | (c) H_3PO_4 | (d) KCl |
| (e) NaOH | (f) NaH | (g) Li_3N | (h) KNaCO_3 |
| (i) K_2O | (j) K_2MnO_4 | (k) $\text{K}_2\text{Cr}_2\text{O}_7$ | |

3.2 Coordination compounds

We know that a coordination compound consists of a metal centre and a set of ligands bonded to it. We also know that a neutral compound or a complex ion does not dissociate into its components when dissolved in a solvent (see, lesson 1). There are three types of coordination compounds/complex ions. For example,

1. **Neutral complexes**, *e.g.* $[\text{CoCl}_3(\text{NH}_3)_3]$, $[\text{CoH}(\text{CO})_3]$ - In a neutral complex, the number of monoanionic ligands coordinated to the metal is equivalent to its oxidation number. Neutral complexes do not produce ions when dissolved in a solution.
2. **Complex cations**, *e.g.* $[\text{V}(\text{NH}_3)_6]^{3+}$, $[\text{Ag}(\text{NH}_3)_2]^+$
3. **Complex anions**, *e.g.* $[\text{CoCl}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$, $[\text{MnO}_4]^-$

A complex cation or anion must accompany an anion(s)/cation(s) to neutralize the charge of the cation/anion. Before we consider naming of coordination compounds we need to look at the types of ligands and their IUPAC names.

3.3 Ligands

Generally, there are two types of ligands found in coordination compounds. They are,

1. **Anionic** ligands (negatively charged ligands), *e.g.* Cl^- , SO_4^{2-} .
2. **Neutral** ligands, *e.g.* CO , NH_3 .

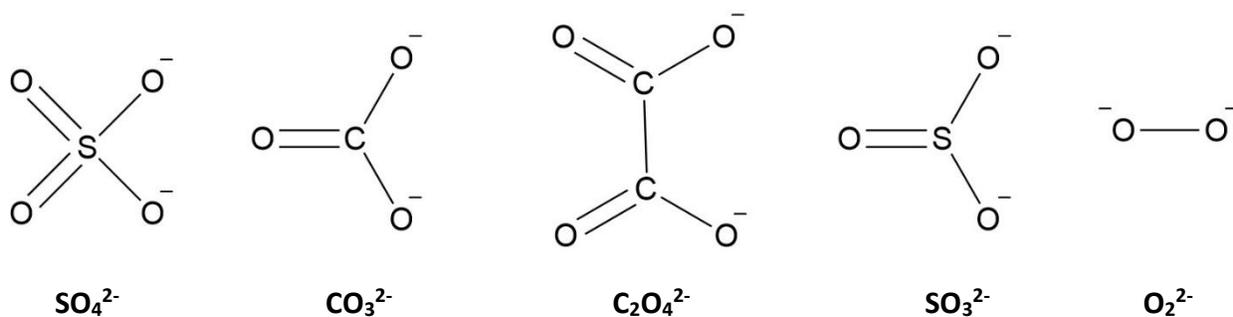
Anionic ligands

Names of the anionic ligands (negatively charged ligands) are given below. When naming coordination compounds, the names of anionic ligands end in o. The **coordinating atoms** are in **bold**.

Ligand	IUPAC name	Ligand	IUPAC name
F ⁻	fluorid <u>o</u>	SO ₄ ²⁻	sulphat <u>o</u>
Cl ⁻	chlorid <u>o</u>	S ₂ O ₃ ²⁻	thiosulphat <u>o</u>
Br ⁻	bromid <u>o</u>	SO ₃ ²⁻	sulphit <u>o</u>
I ⁻	iodid <u>o</u>	CO ₃ ²⁻	carbonat <u>o</u>
H ⁻	hydrid <u>o</u>	C ₂ O ₄ ²⁻	oxalat <u>o</u>
HO ⁻	hydroxid <u>o</u>	NH ₂ ⁻	amid <u>o</u>
N≡C-S ⁻	thiocyanat <u>o-κS</u>	NH ²⁻	imid <u>o</u>
S=C=N ⁻	thiocyanat <u>o-κN</u>	N ³⁻	nitrid <u>o</u>
O ₂ N ⁻	nitrit <u>o-κN</u>	N ₃ ⁻	azid <u>o</u>
O=N-O ⁻	nitrit <u>o-κO</u>	CH ₃ ⁻	methyl/ methanid <u>o</u>
S ²⁻	sulfid <u>o</u>	CH ₃ CH ₂ ⁻	ethyl /ethanid <u>o</u>
HS ⁻	sulfanid <u>o</u>	C ₆ H ₅ ⁻	phenyl
CH ₃ O ⁻	methoxid <u>o</u>	N≡C ⁻	cyanid <u>o</u>
CH ₃ COO ⁻	acetat <u>o</u>	O ₂ ²⁻	peroxid <u>o</u>
O ²⁻	oxid <u>o</u>	O ₂ ⁻	superoxid <u>o</u>

You can see some ligands have only one negative charge on the donor atom (*e.g.* Cl⁻, H⁻, HO⁻ *etc.*) and they are called *monodentate* or *unidentate* ligands. These ligands make **only one attachment** to the metal.

Some ligands such as SO₄²⁻, CO₃²⁻, C₂O₄²⁻, SO₃²⁻ and O₂²⁻ have **two** negative charges on two donor atoms thus they are called dianionic ligands. Since they can form two attachments to a metal centre they are called bidentate ligands.



Neutral Ligands

Names of common neutral ligands are given below. The **coordinating atoms** are in **bold**.

Ligand	IUPAC name
H ₂ O	aqua
N H ₃	ammine
C O	carbonyl
N O	nitrosyl
N ₂	dinitrogen
O ₂	dioxygen
CH ₃ C N	acetonitrile
CH ₃ N H ₂	methylamine

3.4 The IUPAC rules

Earlier we discussed the naming of anionic and some neutral ligands according to the IUPAC (International Union of Pure and Applied Chemistry). Some of the IUPAC rules that are important at the foundation level are given below.

1. When naming a salt, first name the cation then the anion.

Q: Give the IUPAC name of $[\text{Ag}(\text{NH}_3)_2]\text{Br}$

A: Diamminesilver(I) bromide

You know that $[\text{Ag}(\text{NH}_3)_2]\text{Br}$ consists of the cation $[\text{Ag}(\text{NH}_3)_2]^+$ and the anion Br^- . Note that there is a gap between the names of the cation and the anion; the word **ammine** has two m's. The prefix **di** indicates the presence of **two** NH_3 ligands.

2. When naming a complex molecule/ion, name the ligands first in the alphabetical order regardless of their charge, then write the name of the metal followed by the oxidation number of the metal in roman numerals.

Q: Give the IUPAC name of $[\text{NiBrCl}(\text{NH}_3)(\text{CO})]$

A: Amminebromidocarbonylchloridonickel(II)

Here, the ligands are listed in the alphabetical order; the oxidation number of Ni is +2 (or +II) and it is given in parentheses. Note that there are not any **gaps** within the name of a complex molecule/ion.

3. When naming complex anions, the name of the central metal ends in **ate**. For example, scandium becomes scandate; vanadium becomes vanadate; titanium becomes titanate; chromium becomes chromate.

There is no special ending for complex cations or neutral complexes (see examples given under rules 1 and 2).

Q: Give the IUPAC name of $[\text{ZnCl}_4]^{2-}$

A: Tetrachloridozincate(II)

4. When there are several ligands of the same kind, the prefixes *di*, *tri*, *tetra*, *penta*, *hexa*, *hepta*, *octa*, *nona*, *deca*, ... are used with the name. For example,
When there are 2 ammine ligands, *i.e.* $(\text{NH}_3)_2$, the name should include diammine
When there are 3 carbonyl ligands, *i.e.* $(\text{CO})_3$, the name should include tricarbonyl
When there are 4 chloride ligands, *i.e.* $(\text{Cl})_4$, the name should include tetrachlorido

Q: Give the IUPAC name of $[\text{CoCl}_3(\text{NH}_3)_3]$

A: Triamminetrichloridocobalt(III)

5. Prefixes are disregarded when alphabetizing the ligands.
 $[\text{CoFl}_2(\text{NH}_3)_3]$ = triamminefluorodiodidocobalt(III)

3.5 Naming of complex cations and neutral complexes

We know how to name simple inorganic salts (see section 3.1). Let us name some of the complex cations and neutral compounds according to IUPAC rules. Remember that the naming of complex anions is different to those of complex cations and neutral compounds (see section 3.6).

Q: Give the IUPAC names of the following complex cations/neutral complexes.

- (a) $[\text{V}(\text{NH}_3)_6]^{3+}$ (b) $[\text{MnBr}(\text{CO})_5]$
(c) $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]\text{SO}_4$ (d) $[\text{CoCl}(\text{CN})(\text{NO}_2)(\text{NH}_3)_3]$

- A: (a) Hexaamminevanadium(III) ion
(b) Bromidopentacarbonylmanganese(I)
(c) Pentaquahydroxidoiron(III) sulfate(VI) ; $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]\text{SO}_4$ is a salt; the complex cation is named first, then a gap, and the name of the anion.
(d) Triamminechloridocyanidonitrito-κN-cobalt(III)

3.6 Naming of complex anions

In section 3.5, we considered the naming of complex cations and neutral complexes. Now, we will consider the naming of complex anions. According to IUPAC rules, the name of the metal centre in a complex anion should end in *ate*.

Q: Give the IUPAC names of the following complex anions.

- (a) $[\text{TiCl}_5]^-$ (b) $[\text{VCl}_6]^{2-}$
(c) $[\text{MnO}_4]^-$ (d) $[\text{Fe}(\text{CN})_6]^{4-}$
(e) $[\text{CoCl}_4]^{2-}$ (f) $[\text{Ni}(\text{CN})_4]^{2-}$
(g) $[\text{CuI}_4]^{2-}$

- A: (a) Pentachloridotitanate(IV) ion (e) Tetrachloridocobaltate(II) ion
(b) Hexachloridovanadate(IV) ion (f) Tetracyanidonickelate(II) ion
(c) Tetraoxidomanganate(VII) ion (g) Tetraiodidocuprate(II) ion
(d) Hexacyanidoferrate(II) ion

Summary

- When naming simple acids, the *oxidation number* of the *non-metal* (e.g. N, S, C) is given in brackets.
- When naming simple salts, write the name of the cation first with the oxidation number of the metal in brackets followed by the name of the anion with the oxidation number of the non-metal in brackets. The oxidation number of the cation or the anion is not given when it shows only one oxidation state. The name of the anion ends with **ide** or **ate**
- When naming a salt, first name the cation then the anion.
- When naming a complex molecule/ion, name the ligands first in the alphabetical order **regardless of their charge**, then, write the name of the metal followed by the oxidation number of the metal in **roman numerals**. Prefixes are disregarded when alphabetizing the ligands.
- When naming complex anions, the name of the central metal ends in **ate**.
- When there are several ligands of the same kind, the prefixes *di*, *tri*, *tetra*, *penta*, *hexa*, *hepta*, *octa*, *nona*, *deca*, ... are used with the name.



Learning Outcomes

Once you have finished studying this lesson you should be able to

- name simple inorganic compounds.
- explain the IUPAC rules.
- write the IUPAC name of a given coordination compound, complex cation or complex anion.
- write the chemical formula of a coordination compound from its IUPAC name.



Activity

23. What is meant by “complex cation” and “complex anion”? Write three examples for each.
24. Write the formulae of complex cations/anions with the octahedral geometry containing Co^{2+} , ammonia and chloride (if any).
25. Give the IUPAC names of the following compounds/complex ions.
- (a) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (b) $\text{K}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
- (c) $[\text{Mn}(\text{CH}_3)(\text{CO})_5]$ (d) $[\text{Fe}(\text{NCS})][\text{CuCl}_4]$
- (e) $\text{NaFe}[\text{Fe}(\text{CN})_6]$ (f) $\text{K}_2\text{Cu}[\text{Fe}(\text{CN})_6]$
- (g) $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$
26. Give the chemical formula of each of the following compounds.
- (a) Triaquadinitrito- κN -nitrito- κO -cobalt(III)
- (b) Potassium hexacyanonickelate(II)
- (c) Ammonium hexachloridoplatinate(IV)
- (d) Dibromidotetraammineplatinum(IV) nitrate
- (e) Potassium tetrafluoridooxidochromate(V)
- (f) Dichloridodi(methylamine)copper(II)
-
-

4. Reactions of 3d-elements

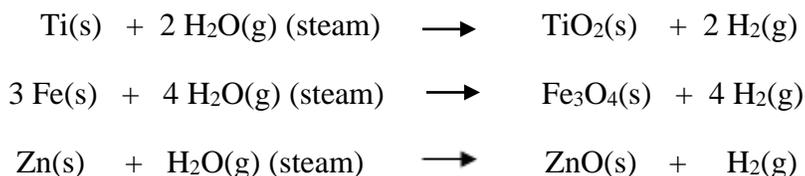
Introduction

In this lesson, we will consider some basic reactions of 3d-elements particularly their reactions with water, air (oxygen), halogens and common acids and bases. Unlike s-block elements, d-elements show variable oxidation states and form coloured compounds.

4.1 Reactions with water

We know that most electropositive alkali metals react violently with water to give hydrogen and metal hydroxides. More electropositive alkaline earth metals such as Ca, Sr and Ba react slowly with water to give hydrogen and metal hydroxides, but beryllium and magnesium do not react with water at room temperature. Titanium metal is coated with an oxide layer that usually makes it inactive, but Ti reacts with steam to give titanium(IV) oxide (TiO₂) and hydrogen.

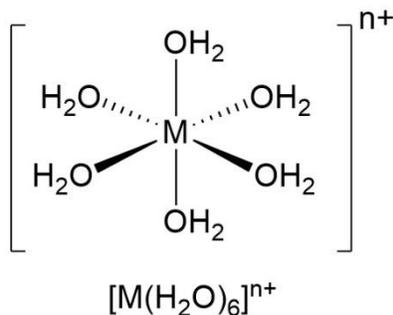
Air-free water has little effect upon iron metal, but, it reacts in moist air by oxidation to give a hydrated iron oxide. This does not protect the iron surface to further reaction as it flakes off, exposing more iron metal to oxidation. This process is called rusting. Iron and zinc react with steam to form metal oxides and hydrogen as shown below.



Vanadium, chromium, nickel, cobalt and zinc do not react with water under normal conditions. Transition metals such as copper (Cu), silver (Ag), gold (Au) and platinum (Pt) do not react with steam or water.

Aqua complexes

Transition metal salts dissolve in water to give aqua complexes, in which water molecules act as an oxygen donor ligand. Divalent (M^{2+}) and trivalent (M^{3+}) transition metal centres form octahedral hexaaqua-complexes of the type $[M(H_2O)_6]^{n+}$ ($n = 2, 3$, $M = Cr, Mn, Fe, Co, Ni, Cu, Zn$).



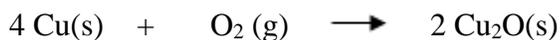
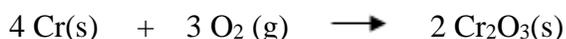
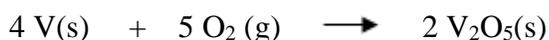
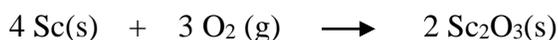
Activity

27. What is meant by rusting of iron? What are the iron containing compounds formed during this process?
-
-

4.2 Reactions with oxygen

We know that all alkali metals react with oxygen. *3d*-Elements react with oxygen to form metal oxides. The composition of the oxide depends on the oxidation state of the metal. Scandium metal tarnishes in air and burns readily in oxygen to form scandium(III) oxide, Sc_2O_3 . Titanium too burns in oxygen to give a white flame and titanium dioxide, TiO_2 . Upon heating, vanadium metal reacts with excess oxygen to form vanadium(V) oxide V_2O_5 . This may be contaminated with other vanadium oxides. Note that vanadium can form four oxides (Table 5). Chromium metal does not react with air or oxygen at room temperature, but at high temperature it gives Cr_2O_3 . Manganese is not particularly reactive to air despite it is a little more electropositive than its neighbours in the Periodic Table. Manganese burns in oxygen to form Mn_3O_4 .

Some examples are given below





Activity

28. Manganese burns in oxygen to form Mn_3O_4 . Write a balanced equation for this reaction.

The known metal oxides of the $3d$ -elements are given in Table 5. You may notice that Ti, V, Cr and Mn could form three to four binary metal oxides. The lowest and highest oxidation states of the metal are +1 and +7, respectively.

Table 5: Simple binary metal oxides of 3d-elements (O.N. = Oxidation number)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	O.N.
								Cu_2O		+1
	TiO	VO		MnO	FeO		NiO	CuO	ZnO	+2
Sc_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_3O_4				+3
	TiO_2	VO_2	CrO_2	MnO_2			NiO_2			+4
		V_2O_5								+5
			CrO_3							+6
				Mn_2O_7						+7



Activity

29. Determine the oxidation state of V in the four oxides of vanadium given in Table 5.

4.3 Reactions with halogens

Like s - and p -block elements, the $3d$ -elements react with halogen to form metal halides. For example, scandium is very reactive towards the halogens (F_2 , Cl_2 , Br_2 and I_2) and burns to form the trihalides ScF_3 , ScCl_3 , ScBr_3 and ScI_3 respectively.



Titanium also reacts with the halogens upon warming to form titanium(IV) halides: $\text{TiF}_4(s)$ (white), $\text{TiCl}_4(l)$ (colourless), $\text{TiBr}_4(s)$ (orange) and $\text{TiI}_4(s)$ (dark brown). The reaction with fluorine requires heating at temperatures above 200°C .



Chromium metal does react with the halogens under mild conditions to form chromium(III) halides: $\text{CrF}_3(\text{s})$ (green), $\text{CrCl}_3(\text{s})$ (red-violet), $\text{CrBr}_3(\text{s})$ (very dark green) and $\text{CrI}_3(\text{s})$ (very dark green).



Chromium metal reacts with fluorine at 400 °C and 200-300 atmospheres to form chromium(VI) fluoride, CrF_6 (yellow). The red chromium(V) fluoride, CrF_5 , is also known.

The fluorides of the 3d-elements are given in Table 6. Ni, Cu and Zn form difluorides. Iron and cobalt form both difluorides and trifluorides.

Table 6: Simple binary transition metal fluorides of 3d-elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	O.N.
		VF_2	CrF_2	MnF_2	FeF_2	CoF_2	NiF_2	CuF_2	ZnF_2	+2
ScF_3	TiF_3	VF_3	CrF_3	MnF_3	FeF_3	CoF_3				+3
	TiF_4	VF_4	CrF_4	MnF_4						+4
		VF_5	CrF_5							+5
			CrF_6							+6

4.4 Reactions with acids

Most of the 3d-elements react with mineral acids. Scandium metal dissolves readily in dilute hydrochloric acid to form solutions containing the hydrated Sc(III) ion together with hydrogen gas, H_2 . As you know, the hydrated Sc(III) ion or $\text{Sc}^{3+}(\text{aq})$ is present as the complex ion $[\text{Sc}(\text{OH}_2)_6]^{3+}$.



Other metals react similarly to give hydrogen and the corresponding salt as shown below.

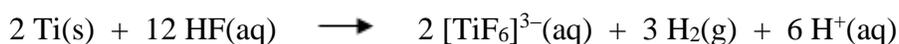


Cobalt metal dissolves slowly in dilute sulphuric acid to form solutions containing the aquated Co(II) ion together with hydrogen.

Iron metal dissolves readily in dilute sulphuric acid in the absence of oxygen to form solutions containing the hydrated Fe(II) ion together with H₂. If oxygen is present, some of the Fe(II) oxidizes to Fe(III).



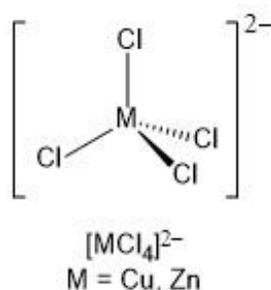
Dilute aqueous hydrofluoric acid, HF, reacts with titanium to form the complex anion [TiF₆]³⁻ together with hydrogen, H₂.



Titanium metal does not react with mineral acids at ambient temperature but does react with hot hydrochloric acid to form titanium(III) complexes.

Reactions of acids with simple salts

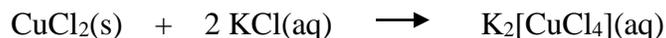
Simple divalent and trivalent transition metal salts dissolve in concentrated acids (HX) to give tetrahedral complex anions of the type [MX₄]²⁻ or [MX₄]⁻.



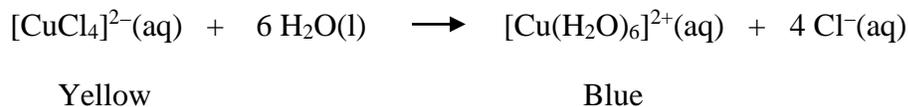
Some examples are given below.



[CuCl₄]²⁻ can also be made by reacting CuCl₂ with chlorides of alkali metals.

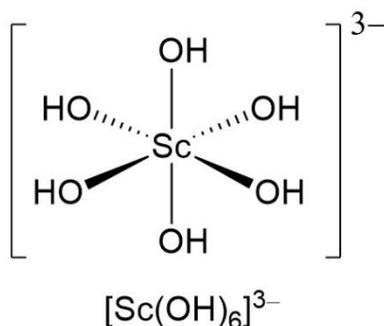
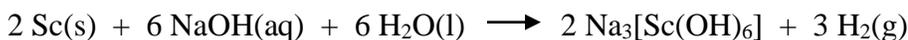


Upon dilution with water the yellow $[\text{CuCl}_4]^{2-}$ ion can be converted into the blue aqua complex ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.



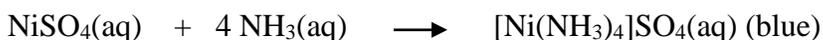
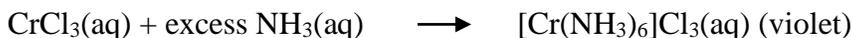
4.5 Reactions with bases

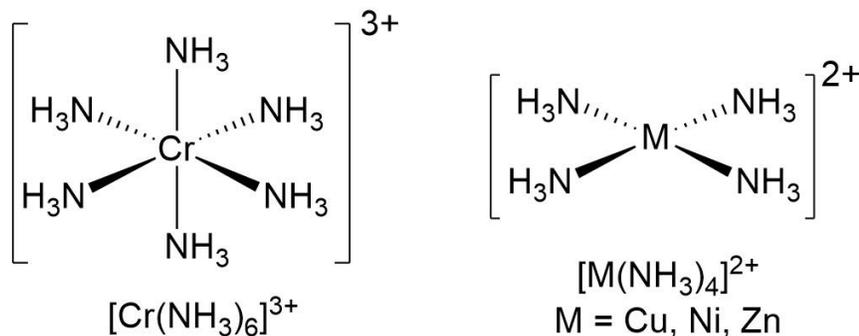
Generally, *3d*-elements are not reactive towards alkaline solutions. Scandium reacts with NaOH to give $\text{Na}_3[\text{Sc}(\text{OH})_6]$ and hydrogen.



Titanium does not appear to react with alkaline solutions under normal conditions, or even with hot solutions. Vanadium metal is resistant to attack by molten metal hydroxide. Nickel does not react with aqueous sodium hydroxide.

Reactions of simple salts with aqueous ammonia or NaOH

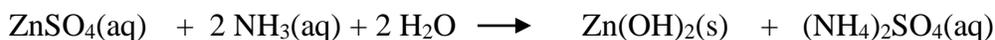
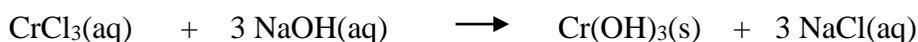




ZnO dissolves in aqueous NaOH to give $\text{Na}_2[\text{Zn}(\text{OH})_4]$.



Most of the aqua complexes of transition metals react with aqueous NaOH or aqueous NH_3 to precipitate the corresponding metal hydroxides. For example



Summary

- Most electropositive alkali metals react violently with water to give hydrogen and metal hydroxides.
- Transition metal salts dissolve in water to give aqua complexes, in which water molecules act as an oxygen donor ligand.
- Like *s*- and *p*-block elements, the *3d*-elements react with halogen to form metal halides. The composition of the halide depends on the oxidation state of the metal. For example, scandium forms the trihalides ScF_3 , ScCl_3 , ScBr_3 and ScI_3 respectively.
- Most of the *3d*-elements react with mineral acids, *e.g.* scandium metal dissolves readily in dilute hydrochloric acid to form hydrated Sc(III) ions and hydrogen gas.
- Most of the aqua complexes of transition metal react with aqueous NaOH or aqueous NH_3 to precipitate the corresponding metal hydroxides.



Learning Outcomes

At the end of this lesson you should be able to

- write chemical equations for reactions of transition metal centres with water, oxygen, halogens, acids and bases.
- suggest preparation methods for aqua-complexes and complexes containing ammonia and halide ions.



Activity

30. Give the molecular formulae of the three binary oxides of titanium. Which titanium oxide is formed when titanium metal is reacted with steam?
 31. Name three transition metals which do not react with steam?
 32. Which two *3d*-elements form only one type of metal oxide?
 33. Which *3d*-element forms a metal oxide of the type M_2O ?
 34. Which *3d*-element forms a metal oxide of the type M_2O_5 ?
 35. Which *3d*-element forms a metal oxide of the type M_2O_7 ?
-
-

5. Extraction and uses of transition metals

Introduction

During lessons 1 to 4 we discussed the chemistry of *d*-block elements covering their physical, chemical and catalytic properties, and the nomenclature of metal complexes. Transition metals play many important roles, for example, haem unit is the oxygen carrier in humans, most of the *3d*-elements are found in biological systems particularly in the active sites of enzymes; vitamin B₁₂ contains a cobalt centre. In this lesson, we will briefly study the methods used for extraction of transition metals and their uses, particularly of iron and copper.

5.1 Occurrence

Iron (Fe) is the most abundant *3d*-element in the earth's crust. It is about 6% of the total crustal composition. The next most abundant *3d*-elements are titanium (0.6%) and manganese (0.1%) while the remainder (V, Cr, Co, Ni and Cu) are rare and sparsely distributed (less than 0.01%).

The majority of the *3d*-elements occur as their oxides, hydrated oxides, carbonates, sulfates and arsenates. The principal minerals and other sources of *3d*-elements are given in Table 7.

Table 7: Occurrence of the first-row transition elements

Metal	Mineral sources
Sc	Thortveitite ScSi_2O_7
Ti	Rutile TiO_2 , ilmenite FeTiO_3
V	Partronite (complex sulphide); vanbadinite $\text{Pb}_5(\text{VO}_4)_3\text{Cl}$; camotite $\text{K}(\text{OU}_2)\text{VO}_4 \cdot 1.5\text{H}_2\text{O}$
Cr	Chromite FeCr_2O_4 ; crocoite PbCrO_4 ; chrome ochre Cr_2O_3
Mn	As the silicate; pyrolusite MnO_2 ; hausmannite Mn_3O_4 ; rhodochrosite MnCO_3
Fe	Haematite, Fe_2O_3 ; magnetite Fe_3O_4 . limonite $\text{FeO}(\text{OH})$; siderite FeCO_3 ; pyrites FeS_2
Co	Smallite CoAs_2 ; cobailite CoAsS ; linnaeite Co_3S_4 ; in association with Ni in arsenic-containing ores
Ni	Laterites such as gamierite $(\text{Ni}, \text{Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$ and nickeliferous limonite $(\text{Fe}, \text{Ni})\text{O}(\text{OH})_n\text{H}_2\text{O}$; garnierte $(\text{Ni}, \text{Mg})_6\text{Si}_4\text{O}_{10}(\text{OH})_8$; sulphides such as pentlandite $(\text{Ni}, \text{Fe})_9\text{S}_8$; associated with Cu, Co and other precious metals in combination with As, Sb and S
Cu	Chalcopyrite CuFeS_2 ; copper glance or chalcocite Cu_2S ; cuprite Cu_2O ; malachite $\text{Cu}_2\text{CO}_3(\text{OH})_2$
Zn	Zinc blende (ZnS) ; smithsonite (ZnCO_3)

A comparison of the abundances of the 3d-elements in the earth's crust is given in the Table 8.

Table 8: Abundance of some elements in the earth's crust

Element	Abundance	Element	Abundance
O	46	Cl	0.1
Si	28	Cr	0.04
Al	8.1	C	0.03
Fe	5.1	V	0.02
Ca	3.6	Ni	0.008
Na	2.9	Cu	0.007
K	2.6	Co	0.002
Mg	2.1	Pb	0.001
Ti	0.6	Sc	0.0005
Mn	0.1	Zn	0.0001

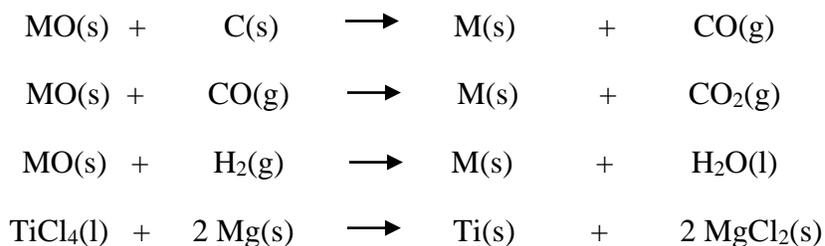
Oxygen, silicon and aluminium are the most abundant elements present in the earth's crust. Ca, Na, K and Mg are the most abundant s-block elements present in the earth's crust. Ca, K, Na and Mg are the most abundant metal ions present in a human body.

Q: What are the four most abundant elements in the human body?

A: H, O, C and N.

5.2 Methods of extraction

Transition metals (M) occur mainly as sulphides and oxides. The least reactive (*e.g.* Cu, Au, Pt) are also found native (*i.e.* uncombined). Reduction of the metal ore is carried out with carbon or carbon monoxide, hydrogen and with a reactive metal as shown below.



The following steps may be involved in the extraction.

1. The first step of the extraction of a metal from its ore involves a concentration of the ore. Various processes are used to separate the ore from unwanted rock *etc.* Sometimes floatation is used - a stream of water carries away debris and leaves the denser ore behind.
2. Sulphide ores are usually roasted to convert them into corresponding oxides.
3. The purified ore (metal oxides or halides) must be reduced to the metal. The choice of reducing agent (*e.g.* C, CO, H₂, Al, *etc.*) is governed by economic as well as the chemical factors and it also depends on the required purity of the metal.
4. When coke is used as a reducing agent, carbon is present as a major impurity. Carbon is removed by heating the impure metal in a stream of air. Further purification may be achieved by electrolysis (*e.g.*, Cu, Ag, Cr).

Extraction of iron

Iron is one of the most important metals. It occurs in nature as oxides or sulphides for example haematite Fe₂O₃; magnetite Fe₃O₄; iron pyrites FeS₂. Iron is obtained by the reduction of its oxides with carbon monoxide. The iron ore contains haematite, *i.e.* Fe₂O₃. Reduction of Fe₂O₃ to Fe by carbon monoxide takes place in a blast furnace at temperatures as high as 800-2000°C.

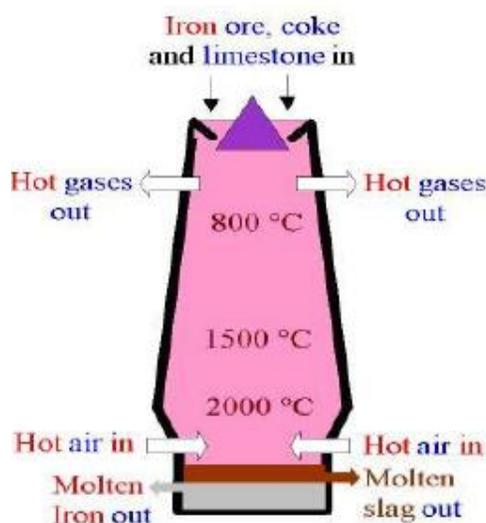
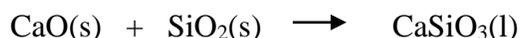


Figure 6: Key steps in a blast furnace (from reference 7)

The furnace is charged with a mixture of limestone, coke and iron source. Air is introduced under pressure near the bottom of the furnace, where the coke combines with oxygen to produce CO. This is an exothermic process, which helps to provide energy to keep the furnace running. The reason for adding limestone is to generate CaO.



CaO reacts with silica present in the ore to produce molten CaSiO₃, which is removed near the bottom of the furnace.



The liquid iron is taken off at the bottom of the furnace which is then cast into moulds. It is called pig iron, as it is not pure. Normally most of the molten iron is turned into steel. This is done by passing oxygen through the impure molten iron. The impurities such as carbon and phosphorous are oxidized into their oxides which escape from the melt either as gases or by being absorbed into slag. The amount of carbon present in the iron determines the nature of iron.

Extraction of copper

The commonest ore of copper is chalcopyrite (CuFeS₂). Copper can be extracted by two principal methods.

1. Pyrometallurgical method – the extraction from sulphide ores.
2. Hydrometallurgical method – recovery of copper from chemical solution (Cu²⁺) by means of solvent extraction (concentration of Cu²⁺ ions using a complexing agent) followed by electrolysis.

Pyrometallurgical method

Extraction of copper from sulphide ores consists of four main stages – (i) mining (digging and collecting the raw materials), (ii) milling (grinding the raw materials after removing unwanted materials) (iii) smelting, and (iv) refining.

Smelting

The concentrated ore is heated strongly with silicon dioxide (silica) and air or oxygen in a furnace or a series of furnaces.

The copper(II) ions in the chalcopyrite are reduced further to copper(I) sulphide (which is further reduced to copper metal in the final stage).

During this process, the iron in the chalcopyrite is converted into an iron(II) silicate slag which is removed.

Most of the sulphur in the chalcopyrite turns into sulphur dioxide gas. This is used to make sulphuric acid *via* the contact process.

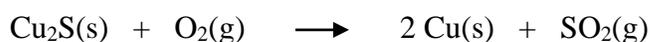
Refining

This is the final stage in the process for obtaining high grade copper by electrochemical methods.

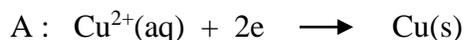
An overall equation for this series of steps is given below.



The copper(I) sulphide produced is converted to copper with a final blast of air.



Q : Write the cathodic and anodic reactions for the above electrolytic refining



5.3 Alloys

A number of *d*-block elements are used extensively for structural purposes in the form of alloys.

An alloy is a uniform mixture of a metal with one or more other elements. An alloy has properties different to its constituent metals. An alloy containing iron as the principal constituent is known as steel. There are two types of steel. Carbon steel and alloy steel. Carbon steel accounts for about 90% of all steel production.

Carbon steel

There are three types of carbon steels depending on the percentage of carbon present -

- (i) mild steel
- (ii) medium steel
- (iii) high carbon steel.

The hardness of carbon steel increases as you increase the amount of carbon.

Table 9: Carbon content and uses of carbon steel

Types of carbon steel	% of carbon	Uses
Mild steel	0.2	General engineering, motor car bodies, wire, piping, nuts and bolts
Medium steel	0.3 – 0.6	Beams and grinders, springs
High carbon steel	0.6 – 1.5	Drill bits, knives, hammers, chisels

Alloy steels

Alloy steels contain iron, carbon and one or more other metals such as Al, Cr, Co, Mo, Ni, Ti, W and V. Stainless steels contain other metals such as Cr and Ni. Tool steels contain W or Mn. Addition of transition metals to iron improves the hardness of the metal and makes the alloy corrosion resistant. The compositions of some common alloys of steels are given below.

Stainless steel - Fe (73%), Cr (18%), Ni (8%), and C (1%)

Tungsten steel - Fe (81%), W (18%), and C (1%)

Cobalt steel - Fe (90%), Co (9%), and C (1%)

Manganese steel - Fe (86%), Mn (13%), and C (1%)

Copper alloys

Copper is used in a wide variety of alloys. The most important ones are given in Table 10.

Table 10: Compositions of some alloys

Alloy	Composition
Brass	Cu and Zn (5 – 45%)
Bronze	Cu and Sn (1 – 15%)
Aluminium Bronze	Sn and Al (1 – 15%)
Phosphor Bronze	Cu, Sn and P (ca 1 %)
Cupro nickel	Cu and Ni (10 – 30%)

Duralumin contains Al (95%), Cu (4%) and other metals. Pewter contains Sn (70-99%) and Cu or Pb (1-15%).

5.4 Uses of 3d-elements and their compounds

Scandium

Sc is not widely used because of its rarity, but it is found in some electronic devices, such as high intensity lamps. The radioactive isotope (Sc-46) is used as a tracing agent in refinery crackers for crude oil.

Titanium

Titanium is less dense than other *d*-block elements. Ti metal and its alloys with Al are extensively used in the aircraft industry (manufacture of aircraft missiles and jet engines). Ti has better corrosion resistance than stainless steel. TiCl_4 and TiCl_3 are used as co-catalysts in the polymerization of alkenes. TiO_2 is used as a white pigment in the manufacture of paints, paper, plastics, cosmetics, synthetic fibres and textiles. Ti is as strong as steel, but 45% lighter. It is 60% heavier than Al, but twice as strong.

Vanadium

V_2O_5 is used as a catalyst for the oxidation of SO_2 to SO_3 . Ferrovandium alloy (50% Fe) is used for springs and high speed cutting tools.

Chromium

Ferrochrome alloy is used to make stainless steel (12-26% Cr) and tool steels (3-6% Cr); Cr is used as an electroplated protective coating. Cr_2O_3 is used as a green pigment; chrome-green, chrome-orange, chrome-yellow and chrome-red are all pigments based on PbCrO_4 .

Manganese

KMnO_4 is a strong oxidizing agent in acid solutions. It is also a mild disinfectant.

Iron

Iron is used to manufacture steel, for example, Stainless steel, Manganese steel, Cobalt steel, Tungsten steel. $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (trade name; Nipride) is an inorganic drug used for hyper

tension and vasodilation. Fe or Fe_2O_3 is used as a catalyst for the manufacture of NH_3 from N_2 and H_2 (Haber process).

Cobalt

Its alloys with Cr and W are used for high speed, heavy duty, high-temperature cutting tools. Some salts have been used for centuries to produce brilliant and permanent blue colour in porcelain, glass, pottery, tiles and enamels. Co-60, an artificial isotope is an important gamma ray source and is used as a tracer and a radio therapeutic agent. A solution of cobalt chloride is used as a sympathetic ink.

Nickel

Nickel is used to harden vegetable oils in the manufacture of margarine. Ni is associated with the enzyme hydrogenase and urease. It is used in food processes and pharmaceutical plants where a non-poisonous, non-corrosive metal is required.

Copper

Copper is used - as an electrical conductor; in casting alloys and to prepare coins; as water pipes because of its inertness. Bordeaux $\{\text{CuSO}_4$ and $\text{Cu}(\text{OH})_2\}$ spray is used in agriculture to prevent fungal attack. Mixed oxides of copper are used as superconductors, *e.g.* $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{(4-y)}$.

Zinc

Uses of zinc include coating on iron to prevent it from rusting (galvanizing); making alloys (*e.g.* brass); casting metal parts; as battery electrodes. ZnS is used in making luminous dials, X-ray and TV screens and fluorescent lights. Zn is an essential element in the growth of human beings and animals. ZnO is used in paint, rubber products, soap and cosmetic industries.

Summary

- The two most abundant *3d*-elements in the earth's crust are iron and titanium.
- Iron is commercially extracted from its ores of hematite (Fe_2O_3) and magnetite (Fe_3O_4).
- Iron is manufactured in a blast furnace by the reduction of iron ore with CO. Limestone is added to remove impurities as slag.
- Copper is extracted from chalcopyrite. Ore containing Cu_2S is reduced by heating it in air with silica.

- Uses of $3d$ -elements and their compounds are given.



Learning Outcomes

At the end of this lesson you should be able to

- list mineral resources of $3d$ -elements
- compare the abundance of $3d$ -elements in the earth's crust
- explain the manufacture of iron and copper from their ores
- compare the compositions of alloys based on iron and copper
- list the uses of $3d$ -elements and their compounds



Activity

36. Name two mineral sources of titanium.
 37. Name two copper ores.
 38. Write the chemical composition of
 - (i) chromite
 - (ii) pyrolusite
 - (iii) siderite
 - (iv) cuprite
 39. What are the three most abundant elements in the earth's crust?
 40. What are the four most abundant metals in the human body?
 41. What are the two most abundant $3d$ -elements in the human body?
 42. Describe the industrial process of manufacturing iron from hematite.
 43. List alloys of copper with their constituents.
 44. What are the four stages of manufacturing copper by pyrometallurgical method?
-
-

Abbreviations

(aq)	- Aqueous; dissolved in water
(g)	- Gas state
Δ	- Heat
μ	- Descriptor for a bridging group
ν	- Frequency
(l)	- Liquid state
(s)	- Solid state
b.pt/b.p.	- Boiling point
C.N.	- Coordination number
Cr^{VI}	- Hexavalent Chromium = Cr(IV) = Cr^{6+}
dmg	- Dimethylglyoxime
EDTA^{4-}	- Ethylenediaminetetraacetate ion
eV	- Electron Volt
J	- Joule
L	- Ligand
M	- Metal
M	- Zerovalent metal = M(0) = M^0
M(g)	- Element in gas state
m.pt/m.p	- Melting point
M^+	- Monovalent metal = M(I) = M^{I}
M^{2+}	- Divalent metal = M(II) = M^{II}
nm	- nanometres
O.N.	- Oxidation number
ox^{2-}	- Oxalate ion ($\text{C}_2\text{O}_4^{2-}$)
pm	- Picometres
ppm	- Parts per million
X	- Halogen
Z	- Atomic number

Glossary

Alloys	: Metallic substance made by mixing and fusing two or more metals, or a metal and a nonmetal, to obtain desirable qualities such as hardness, lightness, and strength, <i>e.g.</i> brass, bronze, steel, <i>etc.</i>
මිශ්‍ර ලෝහ	: දෘඩතාවය, සැහැල්ලු බව සහ ශක්තිමත් බව යන අභිමත ලක්ෂණ ලබා ගැනීමට ලෝහ දෙකක් හෝ වැඩි ගණනක්, ලෝහයක් හා අලෝහයක් හෝ විලයනය කර මිශ්‍ර කර සාදනු ලබන ලෝහමය ද්‍රව්‍ය උදා: පිත්තල, ලෝකඩ, වානේ
கலப்புலோகம்	: இரண்டு அல்லது அதற்கு மேற்பட்ட உலோகங்கள், அல்லது உலோகம், மற்றும் அலோகப் பதார்த்தங்களின் சேர்க்கையால் உருவாக்கப்பட்ட உலோகப் பதார்த்தம்.
Basicity	: The state of being a base.
භාෂ්මිකතාවය	: භෂ්මයක් ලෙස පැවතීමේ හැකියාව
மூலத்திறன்	: மூலமாக தொழிற்படும் நிலை
Coordination number	: The number of coordinated atoms surrounding the central metal atom/ion in a complex or crystal.
සංගත අංකය	: සංකීර්ණ සංයෝගයක හෝ ස්ඵටිකයක මධ්‍ය ලෝහ පරමාණුව/අයනය වටා සංගතව බැඳී පවතින පරමාණු සංඛ්‍යාව
இணைப்பு எண்	: ஒரு சிக்கற் சேர்வையில் அல்லது பளிங்கில் உள்ள மையஅணுவை சூழ இணைந்துள்ள அணுக்களின் எண்ணிக்கை
Electrode potential	: The measure of individual potential of a reversible electrode at standard state, (E°)
ඉලෙක්ට්‍රෝඩ විභවය	: සම්මත තත්ව යටතේ දී ප්‍රත්‍යාවර්ත ඉලෙක්ට්‍රෝඩයක විභවය පිළිබඳ මිනුමකි.
மின்வாயமுத்தம்	: நியம நிலையிலுள்ள மீளும் மின்வாயின் தனிப்பட்ட அழுத்த அளவு
Electrolysis	: The process of interchanging of atoms and ions by the removal or addition of electrons from the external circuit.
විද්‍යුත් විච්ඡේදනය	: බාහිර පරිපථයක සිට ඉලෙක්ට්‍රෝන ලබා ගැනීම හෝ පිටකිරීම මගින් අයන සහ පරමාණු හුවමාරුවීමේ ක්‍රියාවලියයි.
மின்பகுப்பு	: வெளிப்புற சுற்றிலிருந்து இலத்திரனை இழத்தல் அல்லது கூட்டல் மூலம் அணுக்களையும் அயன்களையும் இடம் மாற்றிக் கொள்ளும் ஒரு முறை.
Electron configuration	: Specific distribution of electrons in atomic orbitals of atoms or ions.
ඉලෙක්ට්‍රෝනික වින්‍යාසය	: පරමාණුවක හෝ අයනයක කාක්ෂිකවල ඉලෙක්ට්‍රෝන පැතිර ඇති ආකාරයි
இலத்திரனிலையமைப்பு	: அணுக்களினது/அயன்களினது அணுவொழுக்கில் இலத்திரன்களின் குறிப்பிட்ட பரம்பல்.

Electronegativity විද්‍යුත් සෘණතාවය மின்னெதிரியல்பு	: The tendency of an atom to attract shared electrons : බන්ධනයක ඇති ඉලෙක්ට්‍රෝන තමා දෙසට ඇද ගැනීමේ හැකියාවයි. : பங்கிடப்பட்ட இலத்திரன்களை கவரும் அணுக்களின் தன்மை.
Electropositive විද්‍යුත් ධනතාවය மின்னேரියல்பு	: The tendency of an atom to remove valence electrons. : සංයුජතා කවචයේ පවතින ඉලෙක්ට්‍රෝන ඉවත් කිරීමට පරමාණුවක් සතු හැකියාවයි. : வலுவளவு இலத்திரன்களை அகற்றும் அணுக்களின் தன்மை.
Furnace උෂ්මකය உலை	: an enclosed chamber in which heat is produced to generate steam, destroy refuse, smelt or refine ores, etc. : හුමාලය නිපදවීමට, අපද්‍රව්‍ය විනාශ කිරීමට, විරුවීමට හෝ ශුද්ධ කිරීමට තාපය නිපදවනු ලබන සංචාන කුටීරයයි. : கழிவுகளை நீக்குவதற்கு, உருக்குதல் அல்லது தாதுப்பொருட்களை சுத்திகரிப்பதற்கு, ஆவியை உருவாக்குவதற்கு தேவையான வெப்பத்தை உற்பத்தியாக்கும் ஒரு மூடப்பட்ட அறை.
Geometry ජාමිතිය கேத்திர கணித உருவம்:	: The arrangement of a molecule in the space. : අණුවක ත්‍රිමාණ සැකසුම/ව්‍යුහය : ஒரு வெளியிலுள்ள மூலக்கூறின் மூலக்கூறின் ஒழுங்கமைப்பு.
Group number කාණ්ඩ අංකය கூட்ட எண்	: The number of a vertical column in the periodic table; there are 18 groups. : ආවර්තිතා වගුවේ සිරස් තීරුවකට අයත් අංකය. එහි කාණ්ඩ 18 කි. : ஆவர்த்தன அட்டவணையில் நிலைக்குத்து நிரை கூட்டமாகும்
Hydration සජලනය நீரேற்றம்	: The act or process of combining or treating with water. : ජලය සමඟ එකතු වීම හෝ සම්බන්ධ වීමේ ක්‍රියාවලිය : நீருடன் சேர்க்கைஅடையும் தாக்கம்
Hydrolysis ජල විච්ඡේදනය நீர்ப்பகுப்பு	: The breaking down of a chemical compound into two or more simpler compounds by reacting with water. : ජලය සමඟ ප්‍රතික්‍රියා කර රසායනික සංයෝගයක් සරල සංයෝග දෙකක් හෝ කිහිපයක් බවට බිඳ හෙලීම : நீருடன் தாக்கமடைவதன் மூலம் இரசாயனச் சேர்வைகள் 2 அல்லது அதற்கு மேற்பட்ட பகுதிகளாக உடையும் பொறிமுறை.
Isoelectronic සමඉලෙක්ට්‍රෝනික சமவிலத்திரணுக்குரிய	: Several dissimilar atoms or ions with identical electronic configurations. : එකම ඉලෙක්ට්‍රෝනික වින්‍යාසය සහිත විවිධ පරමාණු හෝ අයන : ஒரே மாதிரியான இலத்திரன் நிலையமைப்புக் கொண்ட வேறுபட்ட அணுக்கள் அல்லது அயன்கள்.

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