Transition Metal Chemistry

The term 'transition elements' includes all the elements in the central part of the Periodic Table- between the block of typical metals in Groups I and II and the block of elements mostly non-metals in groups III to Group VIII. This position helps to explain the use of the word 'transition'.

The elements of the first transition series, i.e. the those in the fourth period, show remarkable similarity to each other in their properties and are all metals.

General Characteristics of the Transition Elements

In contrast to the representative metals of Group IA and IIA, most of the transition metals are characterized by the following properties:

1. Hard and relatively dense
2. Relatively high melting and boiling points
3. Several oxidation states
4. Coloured compounds
5. Paramagnetic compounds
6. Weaker reducing agents than the metals of Group IA an Group IIA
7. Act as catalysts, (both the metals and their compounds).

A transition element is a metal which has a wide variation of oxidation states, forms coloured ions, possess catalytic activity, paramagnetism is observed and forms complex compounds.

Thus, generally, transition metals are hard, strong, lustrous, high m.p., high bp., high ΔH_{vap}, malleable, ductile, and good conductors.

Physical properties depend on outer electrons and on the electron arrangement. We generally encounter similarities in physical properties and chemical properties as we go down a particular group in the Periodic Table, rather than as we go across the second or third period, say from Li → F or Na→ Cl. Instead, we generally encounter dissimilarities going across the periodic table. However, in the case of TM's they show a remarkable similarity as we go across the TM series from Ti → Cu, example: atomic radii, IE, mp, bp, oxidation states.

The reason for their similarity of properties is that each additional electron is entering the 3d shell, but the chemistry of these elements is largely due to the 4s electrons. From one transition element to the next, the nuclear charge increases by one unit, and the number of electrons also increases by 1. Since each additional electron enters the 3d shell, it helps to shield the 4s electrons from the increased nuclear charge, with the result that the effective nuclear charge remains fairly constant across the series of transition elements. The size of the atoms and the magnitude of the first ionisation energies are therefore very similar and the elements have comparable electropositivities.

Electron Configuration of the elements

In the hypothetical process of 'building up' atoms by adding electrons and protons one by one the 4s orbitals are filled before the 3d.

Write down the electron configurations, in s, p, d notation for the elements $_{21}Sc$ to $_{31}Zn$.

Write down the shorthand notation, using the symbol of the noble gas for the elements $_{21}Sc$ to $_{31}Zn$.

You have noticed that the atoms of chromium and copper have only one 4s electron, whereas all the others have two. Suggest reasons **why atoms of chromium and copper have only one 4s electron**, whereas all the other elements in the first transition series have two 4s electrons.

For chromium, the $3d^5 4s^1$ configuration is at a lower energy level than $3d^4 4s^2$ because the former has more unpaired electrons. The extra repulsion between paired electrons, as compared to unpaired electrons, outweighs the small energy difference between the 3d and the 4s electrons.

For copper, the $3d^{10} 4s^1$ configuration is more stable than $3d^9 4s^2$ for the same reason. Note: that the so-called 'extra stability of the half-filled sub-shell' is a description of this effect and not an explanation. Thus, there appears to be a certain measure of stability associated with a full d^{10} shell and with a half-filled d^5 shell.

What would you expect to be the electron configurations of molybdenum and silver atoms?

Tranisition metals are often referred to as d block metals. They are defined as elements which form some compounds in which there is an incomplete subshell of electrons.

d-block element: an element that possess an incomplete inner subshell of d-electrons.
(because the inner 3d energy level is being filled up)

Why scandium and zinc are not typical transition metals.
Scandium ($3d^0$ in compounds), and Zinc ($3d^{10}$ in compounds), are not regarded as TM, because all compounds of Sc have an **empty** 3d shell, where as zinc compounds have a **filled** 3d shell. The typical properties of compounds of transition elements are associated with **partly filled d orbitals**. For this reason, scandium and sinc may be excluded from a study of transition elements; however it is convenient to include these metals with the transition metals, on account of the chemical resemblance of their compounds to the transition metals compounds.

Formation of Ions

In the building up of atoms by adding electrons and protons one by one the 4s orbitals are filled before the 3d – you might therefore expect the 3d electrons to be lost first.

3d electrons would be lost first if protons were lost at the same time but, of course in the formation of ions, only electrons are lost, leaving the atoms with an excess positive charge (i.e. greater nuclear charge). This excess charge has the effect of pulling **all** the electrons a little closer and, in the process the **3d orbitals occupy a lower energy level than the 4s**.

This is one consequence of the fact that the 3d and 4s energy levels are fairly close together for the transition elements, as shown in **Diagram I**. At scandium, the effect is that the energy levels are 'inverted' and the energy of the 3d orbitals is less than that of the neutral atoms. This means that the **4s electrons will be lost first** when the ions are formed.

It can also be seen that a number of different electron configurations could be reasonably stable for ions of transition elements, instead of the more usual single stable configuration for other metals. Stable electron arrangements might be expected from the loss of:

1. all 3d and 4s electrons giving a noble gas configuration
2. the 4s electrons only, leaving the 3d untouched,
3. the 4s and some 3d electrons, leaving the 3d sub-shell half-filled

Note, that as the number of electrons lost increases, the stability of the resulting ions usually decreases. However, you see higher oxidation states in covalent structures.

The stability of a particular ion formed depends to some extent on the anion with which it combines. For instance, F^{-1} ion, and to some extent $C1^{-1}$, which are small and not easily polarized, stabilize high oxidation states. On the other hand, I^{-1} and Br^{-1} stabilize lower oxidation states.

The stability of the +2 oxidation state relative to the +3 and higher oxidation states increases from left to right across the series. It reflects the increasing difficulty of removing a 3d electron as nuclear charge increases.

Write electron configuration for the following ions:

Sc^{+3} V^{+3} Fe^{+2} Cu^{+1} Cu^{+2} Fe^{+3}

Mn^{+2} Ni^{+2} Cr^{+1} Zn^{+2} Co^{+3} Ti^{+3}

The Pattern of Oxidation States

The transition metals are often said to exhibit 'variable oxidation state' -these are attributed to the unpaired inner 'd-electrons' which require little promotion energy for use as valency electrons.

The multiple oxidation states of transition elements can be attributed to the availability of d-electrons for bond formation.

Ions with charges greater than 3+ are rarely found, but higher oxidation states than 3 or 4 (in which the electrons may be regarded as 'partially lost' to more electronegative atoms in covalent bonding) are very common in compounds of the transition elements. Higher oxidation states are most often seen in oxides and oxo-anions.

The following table summarises the known oxidation states of elements of the first transition series - the most common states are labelled with an asterix:

Diagram Summary of Common Oxidation States

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
				7*					
			6*	6	6				
		5*	5	5	5	5			
	4*	4	4	4	4	4	4		
3*	3	3	3*	3	3*	3	3	3	
	2	2	2	2*	2*	2*	2*	2*	2*
	1	1	1	1	1	1	1	1	

From the above table the following pattern in oxidation states may be summarised:

1. From Sc to Mn, the maximum oxidation state commonly occurs. This involves loss (or partial loss) of all 4s and 3d electrons giving a noble gas structure.

2. From Mn to Zn, an oxidation state involving only the loss of 4s electrons commonly occurs. This suggests that the removal of the paired 3d electrons is less easy.

The maximum oxidation state is two more than the number of unpaired 3d electrons, i.e. the maximum oxidation state uses only the 4s electrons and unpaired 3d electrons.

<u>Explain why Zn has only one oxidation number, whereas manganese has six.</u>

Zn has a full and stable 3d orbital, so none of the 3d electrons are used in bonding. Only the 4s electrons are used and hence only Zn^{+2} is known. Manganese is $3d^5 4s^2$. It can lose its two 4s electrons to form Mn^{+2} or it can use any of its 5 single electrons for bonding, giving rise, in total, to six different oxidation states.

Coloured Compounds

In general, a substance appears coloured because it absorbs some of the light which falls on it. The light which is then reflected or transmitted to the observers eye is not a complete spectrum of the wavelengths which make up white light, but appears to have a colour complementary to that of the absorbed light. For example, copper sulphate solution appears blue because it absorbs red light.

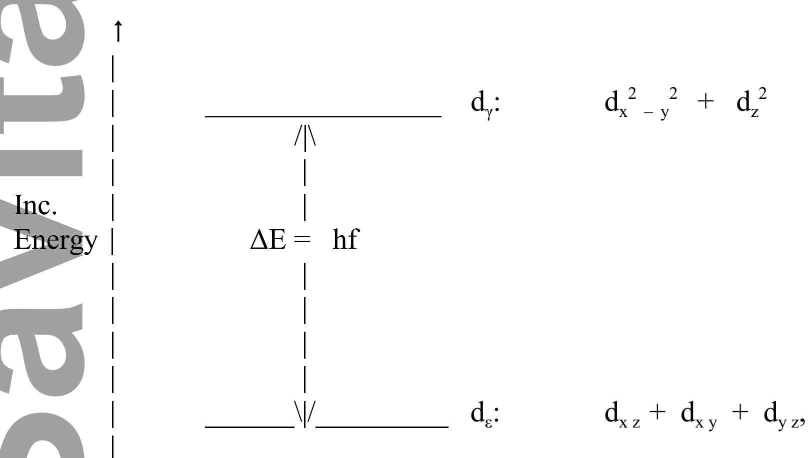
All substances absorb some wavelengths of the electromagnetic spectrum in a variety of ways – this enables us to identify substances by infra-red and ultraviolet spectroscopy. However, the absorption of visible wavelengths always involves promotion of electrons from one energy level to another fairly close.

Although the 3d and 4s levels are generally very close in compounds of transition metals, the gap is usually too large for visible light to cause electron transitions.

The **ligand field theory** also referred to as the **crystal field theory** explains how the presence of ligands causes the five degenerate 3d orbitals, to non-degenerate: i.e. to split into levels with a gap suitable for the absorption of visible light.

In an isolated transition metal atom the five d orbitals are degenerate, i.e. they are all at the same energy level. In a complex ion, the d orbitals differ slightly in energy as a result of overlapping differently with the ligands: they are now non-degenerate. This energy splitting between the two sets of d-orbitals is called the **crystal field splitting** and is represented by the letter Δ.

The d_ε becomes lower in energy than the d_γ orbital. The difference in energy between these two levels is normally such that the visible light can excite an electron from the lower, d_ε level to the higher energy level, d_γ.



Electrons can jump from one d orbital to another if they absorb energy. The frequency of light energy absorbed in these energy transitions is in the visible region of the spectrum, and the ion appears coloured. The reason for the splitting of the d-orbitals is that the spatial arrangement of the d-orbitals (all 5 of them) is not the same as that of the ligands.
When light passes through an aqueous solution of a complex ion, electrons are promoted from the lower of the two energy levels, d_ε, of the 3d orbitals to the higher level, d_γ, absorbing light of

a particular frequency, f. This frequency is related to the energy gap ΔE by Planck's constant 'h' according to the relationship:

$$\Delta E = h f$$

Some electrons fall back again directly, re-emitting the absorbed light, so that the light emerging from the solution is no longer white but coloured.

The energy difference between the two levels varies slightly with different ligands so that complex ions have different colours. The magnitude of energy difference between the two sets of levels, d_ε, and d_γ is a measure of the ligand field strength.

Some ligands lead to a small energy separation of the d-orbitals, while others lead to a large separation, i.e. some ligands create a small crystal field while others create a large field. From experiment it has been found that the separation or 'splitting' of d-orbitals is of the following order:

CN^{-1} > NO_2^{-1} > NH_3 > H_2O > F^{-1} > OH^{-1} > Br^{-1}

large orbital splitting large ΔE strong field ligands	Small orbital splitting Small ΔE Weak field ligands, low energy photons required to induce electron transition

The magnitude of the energy difference depends on:

1. the nature of the ligand and
2. the shape of the complex ion formed.

The greater the energy difference, the greater the tendency of the d-electrons to fall back to the d_ε orbitals.

[Note in octahedral complex ions, i.e. 6 ligands around the central metal ion, M^{+n}, will split the d-orbitals into the same splitting as shown above, however, tetrahedral ligands, i.e. 4 ligands around the central M^{+n}, the splitting pattern is reversed.]

Example: Cu^{+2}

In the solid anhydrous $CuSO_4$, the Cu^{+2} is surrounded by the SO_4^{-2}, the d-orbital splitting is such that the absorption of light by the Cu^{+2} cation is not in the visible spectrum and ∴ the substance appears white.

However, in aqueous solution the Cu^{+2} is surrounded by the H_2O molecules $\longrightarrow$ $Cu(H_2O)_6^{+2}$ – these complex ions absorb light in the visible region and ∴ appear blue.

Upon crystallization, the water molecules remain co-ordinated round the Cu^{+2} ➜ $CuSO_4 \cdot 5H_2O$, ∴ the solid appears blue.

The factors that determine the colour os a complex ion are:

1. The transition metal involved: each has its own characteristic colours.
2. The oxidation number of the transition metal
3. The number of ligands that surround the transition metal ion.
4. The nature of the ligands that surround the transition metal ion.

Why are the following compounds colourless: $ScCl_3$, $ZnSO_4$, $CuCl$?

Sc^{+3} have no electrons in the 3d or 4s orbitals, ∴ electron transitions involving such electrons are not possible. The $Sc^{+3}_{(aq)}$ ion has no d electrons, and is thus colourless.

Zn^{+2} and Cu^{+1} have complete 3d sub-shells, with a d^{10} configuration, no d - d transition is possible, and these ions are colourless. The electron transitions responsible for the colour of transition elements always involve partly filled orbitals.

Formation of Complex Compounds

The transition elements are highly charged, therefore they readily attract polar molecules or ions to form stable complex ions. These complex ions will also be coloured, and the colour will vary depending on the molecules surrounding the central transition element.
For example, $Cu(H_2O)_4^{+2}$ is a pale blue ion in solution, whereas $Cu(NH_3)_4^{+2}$ is a much deeper blue.

Coordination compounds are prevalent both in nature and in chemical laboratories:
—>Dyes containing coordination compounds were used thousands of years ago.
—>The red colour of blood is caused by the presence of hemoglobin, a coordination compound containing Fe(II).
—>Chlorophyll, which is found in plants, is a coordination compound similar in structure to hemoglobin, but containing Mg(II) instead of Fe(II).

The tendency to form complex ions is due to three factors:

1. Unfilled d-electrons that can be used to form bonds.
2. The high – charge density of the nucleus.
3. The small radii of the ions.

The first two factors will allow the elements to attract ions or molecules that are highly electronegative.

Ions with a large positive charge density (intense electric fields), have a strong tendency to interact with ligands such as H_2O, NH_3, and CN^{-1}, all of which have highly electronegative atoms and unshared electron pairs.

In general, the smaller the positive ion and the larger the charge, the greater will be the tendency to form stable complexes. Thus, the relatively large ions of Group IA and Group IIA elements do not have as great a tendency to form stable complex ions as do the smaller, more highly charged ions of the transition elements.

Definition: A complex ion is a central metal ion surrounded by a number of oppositely charged ions or neutral molecules called **Ligands**.
[Ligand originates from the Latin word "ligare" means 'to tie' or 'to bind']

Ligands are Lewis bases, i.e. lone electron pair donors.

Ligands must possess one or more unshared pairs of electrons. Ligands can be neutral molecules or anions, example: NH_3, H_2O, CO, Cl^{-1}, CN^{-1}, OH^{-1}

Transition metal cations are Lewis acids, i.e. lone pair acceptors, they have empty orbitals to accommodate the electrons.

Ligands are linked to the central transition metal cation by co-ordinate covalent bond, a ligand forms a σ-bond with its lone pair with an empty d-orbital on the metal atom or ion.

M^{+n} + $:NH_3$ ⟶ $[M \leftarrow NH_3]^{+n}$

Example: Cu^{+2} + $4\ :NH_3$ ⟶ $[Cu(NH_3)_4]^{+2}$
Central ion — ligand — complex ion— containing 4 coordinate bonds

The transition metal cation and the ligand can exist separately.

Complexes can have an overall charge of positive, negative or zero (i.e. neutral). The number of complexes in high oxidation states is very limited. At lower oxidation states, a variety of ligands can form complexes.

The number of ligand donor atoms that surround a central transition metal cation in a complex is called the **coordination number** of the metal and is related to the :

1. charge, the electronic configuration and the size of the central metal ion,
2. size and shape of the ligands

Greater number of ligands can surround a small, highly charged central metal ion.

The common co-ordination number and the geometry of the complex ions is given below:

2: linear, example: $Ag(NH_3)_2^{+1}$, $CuCl_2^{-1}$ (Recall: *sp* hybridisation, linear)

4: tetrahedral, example $Ni(CO)_4$, $CoCl_4^{-2}$ *(tetrahedral:sp^3)*
or very occasionally square planar, example $Pt(NH_3)_4^{+2}$, $CoCl_4^{-2}$ *(square planar: dsp^2)*

6: octahedral, example $CoCl_6^{-3}$, $Fe(CN)_6^{-3}$, $Cr(H_2O)_6^{+3}$ *(sp^3d^2)*

8: $Mo(CN)_8^{-4}$

[rarely may be odd example 3: HgI_3^{-1} , Or 5: trigonal bipyramidal: $Fe(CO)_5$].

Example: $CoCl_6^{-3}$

```
        Cl
        |    Cl
   Cl   Co
   Cl   |    Cl
        Cl
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Co^{+3}: electron - pair acceptor, Lewis acid, co-ordinate metal ion
Cl^{-1}: electron pair donor, Lewis base, ligand
/ \: coordinate, dative, σ-bond
Co^{+3}: electronic configuration: $[Ar]3d^6\ 4s^0\ 4p^0$
Co in $CoCl_6^{-3}$ electronic configuration: $[Ar]3d^6\ 4s^2\ 4p^6$
coordination number: 6
shape of the complex: octahedral

Some common neutral ligands are given common names:
aqua: H_2O ammine: NH_3 carbonyl: CO ethylenediamine, en

Because all ligands are Lewis bases, they have at least one lone pair of electrons that can be used to form a coordinate covalent bond to a metal ion. The number of co-ordinate covalent bonds formed with the central cation may be classified as:

1 bond → monodentate ligand : H_2O, NH_3, NO_{2-}^{-1}, OH^{-1}
(Latin: dentis —> 'tooth', monodentate: 'one-toothed')

2 bonds → bidentrate : $C_2O_4^{-2}$, ethane-1,2-diamine [en: (NH_2CH_2 - CH_2NH_2)], CO_3^{-2}

3 bonds → tridentate: diethylenetriamine: :$NH_2CH_2CH_2N$:HCH_2CH_2N:H_2

4 bonds → polydentate : EDTA (ethylene-diamine-tetra-acetate: hexadentate)

Ligands that can bond through electron pairs on more than one donor atom are termed as polydentate ligands, example: ethane-1,2-diamine, :NH_2CH_2 - CH_2H_2N:

Polydentate ligands are known as **chelating agents**, they "grasp" a metallic ion so that it is enclosed in a ring-like structure. (FYI: Greek: crab's claws, because their multipoint attachment to a metal ion resembles the grasping of an object by the claws of a crab!!! They act rather like the claws of a crab clamping on to a food morsel.)

By this action, chelating agents are able to deactivate and control metallic ions. Traces of metallic ions in foods and other products often accelerate undesirable oxidation reactions which impair the colour, flavour, clarity, and stability of the product. Chelating agents are often added in small quantities to deactivate the metallic ions.

A **chelate** is defined as a ligand that can form more than one bond to a metal ion, i.e. the ligand has more than one Lewis base site. A polydentate ligand generally gives a more stable complex ion than a monodentate ligand, because the greater the number of bonds, the more difficult it will be to remove the ligand and, ∴ the more stable the complex ion.

Rules for Naming Co-ordination complexes

The name of the complex gives the name and oxidation state for the central metal cation, e.g. cobalt (III), preceded by the name and number of ligands attached to it, e.g., hexaammniecobalt (III) ion: $[Co(NH_3)_6]^{+3}$

1. As with any ionic compound, the cation is named before the anion.

2. In complex ions, the ligands are named before the central metal atom / ion.

3. For mixed ligands, place the name of the ligands in alphabetical order, ignore the prefixes di-, tri-.

4. For same kind of ligands, use the prefix: di-(occasionally bi is used), tri-, tetra, etc.

5. When the central atom / ion is positive or neutral, then the name remains unaltered followed by a Roman numeral for the oxidation number.

6. However, if the complex is an anion, the suffix – ate is added to the name of the central atom followed by Roman numeral for the oxidation state, e.g., zincate and chromate. If the metal has a Latin name, then in the complex anion the Latin name of the metal is used, followed by the suffix –ate e.g. $[Fe (CN)_6]^{-4}$ is hexacyanoferrate (II).
Note: iron: ferrate, Cu: cuprate, Sn: stannate, Ag: argentate, Pb: plumbate,
Au: aurate, Pt: platinate, Mn: manganate, Cr: chromate, V: vanadate, Mn: manganate.
The metal name is not separated from the ligand names by a space.

7. In naming ligands an "o" is added to the root name of the anion, ex. Hydroxo, fluoro, cyano:CN^{-1}, carbonato: CO_3^{-2}, oxalato: $C_2O_4^{-2}$, sulphato: SO_4^{-2}, nitro: NO_2^{-1}, Nitrato: NO_3^{-1}, thiocyanato, SCN^{-1}, thiosulphato: $S_2O_3^{-2}$

The charge remaining on the central atom or ion when the ligands are removed together with their lone pairs is the oxidation number of the metal in the complex.

Assignment

1. Name the following complexes, identify the central ion, the ligand(s) and the co-ordination number and the shape of the complex ion:

$Cu(NH_3)_4^{+2}$	$CrCl(H_2O)_5^{+2}$	$CuCl_4^{-2}$	$Ag(CN)_2^{-1}$
$Co(OH)_2(H_2O)_4$	$(NH_3)_4VF_6$	$Pt(NH_3)_2Cl_2$	$Fe(CO)_5$
$Mn(H_2O)_6^{+3}$,	$[Co(NH_3)_5(SO_4)]$ Br,	CoF_6^{-3},	$Ag(NH_3)_2^{+1}$,
$Fe(CN)_6^{-3}$,	$Ir(NH_3)_3Cl_3$,	$K_4Fe(CN)_6$,	$K_3Fe(CN)_6$,
$Zn(OH)_4^{-2}$	$[Pt(NH_3)_5Cl]Cl_3$	$Pt(NH_3)(Cl)_5^{-3}$	$Pt(NO_2)_4^{-2}$
$K[Pt(NH_3)Cl_5]$	$Cd(CN)_4^{-2}$	$[Co(NH_3)_4SO_4]NO_3$	$[Co(NH_3)_4CO_3]Cl$
$Co(NO_3)_3(NH_3)_3$	$Co(NO_2)_6^{-3}$	$CrCl_2(H_2O)_4^{+1}$	$Ni(CO)_4$
$[Ni(H_2O)_6]SO_4$	$Na_2Co(SCN)_4$	$Co(SCN)_4^{-2}$	K_2PtCl_6
$[Rh(NH_3)_5I]I_2$	$Fe(C_2O_4)_3^{-3}$	$Na[Cr(OH)_4]$	$Al(OH)_4^{-1}$

2. Given the co-ordination numbers shown, write down the formulae and names of the complexion formed between:

   Cu^{+2} and H_2O (C.N = 4) Fe^{+3} and CN^{-1} (C.N = 6)

   Ni+2 and Cl^{-1} (C.N = 4) Ag^{+1} and NH_3 (C.N = 2)

3. Identify four types of bonding in crystals of $CuSO_4.5H_2O$

4. Write the formula for each of the following:
   a. Potassium tetracyanonickelate(II)
   b. Sodium hexafluoroaluminate
   c. Diamminesilver(I) ion

Geometrical Isomerism

This results when the atoms bonded directly to the metal are sequenced in a different order about the metal. Example: diamminedichloroplatinum (II): Pt $(NH_3)_2$ Cl_2

cis	trans
NH_3 Cl	NH_3 Cl
Pt	Pt
NH_3 Cl	Cl NH_3
cis- platin	trans
angle between adjacent ligands = 90^0	angle between opposite angles = 180^0
(used to treat brain tumors)	(physiologically inactive)

Cis- and trans- isomer are different compounds with different properties. Thus, the cis- isomer is a polar molecule and is more soluble in water than the trans. The trans isomer is nonpolar because the two Pt– Cl and the two Pt– NH_3 bond dipoles point in opposite directions and .: cancel.

Draw two isomers for the complex ions with the following formula:

(i) $[Cr(H_2O)_4Cl_2]^{+1}$ (ii) $[Cr(NH_3)_4Cl_2]^{+1}$ (iii) diamminedichlorocobalt(II) (this complex is not tetrahedral)

Competition between Ligands: Displacement reactions and the Stability Constant

Some ligands form stronger bonds than other ligands with a metal ion, example:

$$[Cu(H_2O)_4]^{+2}_{(aq)} + 4Cl^{-1}_{(aq)} \rightleftharpoons [CuCl_4]^{-2}_{(aq)} + 4H_2O_{(l)} \quad K_c = 3.9 \times 10^5\ dm^{12}\ mol^{-4}$$

The equilibrium constant, **Kc**, also known as the **stability constant**, demonstrates this equilibrium is product dominated, indicating that the Cl^{-1} ion is a better ligand than H_2O. The larger the numerical value of the constant Kc, the more product favoured the reaction.

$$[Cu(H_2O)_4]^{+2}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{+2}_{(aq)} + 4H_2O_{(l)} \quad K_c = 1.5 \times 10^{13}\ dm^{12}\ mol^{-4}$$

Thus, the equilibrium is strongly product dominated , NH_3 is a better ligand than H_2O.

Polydentate ligands are better ligands than monodentate ligands, they have higher K_c values.

Catalysis Involving Transition Elements

Recall: a catalyst speeds up a chemical reaction by providing an alternative route with lower activation energy. Clearly, the catalyst must take part in the sequence of reactions, but since the eventual products are the same, the catalyst must be regenerated.

Transition metals have high catalytic activity both as metals in **heterogeneous catalysis** and as ions in **homogeneous catalysis** in solutions.

It is likely that the 3d electrons enable the transition metal catalyst to form temporary bonds with the reactant molecules in heterogeneous catalysis.

In homogeneous catalysis, the existence of a variety of oxidation states for each element explains how the transition metal is able to take part in a sequence of reaction stages and emerge unchanged at the end.

Some examples of catalysis in industry

1. Haber Process: Manufacture of ammonia
   $N_2 + 3H_2 \rightleftharpoons 2NH_3$ — Fe

2. Contact Process: Manufacture of sulphuric acid
   $SO_2 + O_2 \rightleftharpoons 2SO_3$ — V_2O_5

3. Manufacture of antifreeze: ethan-1,2-diol
   $2C_2H_4 + O_2 \rightleftharpoons 2C_2H_4O_2$ — Ag

4. Manufacture of margarine
   RR'C = CR"R'' $\rightleftharpoons$ RR'CHCHR"R'' — Ni

5. Manufacture of nitric acid
   $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$ — Pt

General Examples of Catalysis in the Laboratory

$2H_2O_2 \longrightarrow 2H_2O + O_2$ — MnO_2

$2KClO_3 \longrightarrow 2KCl + 3O_2$ — MnO_2

$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$ — Fe (or $FeBr_3$)

$Zn + 2H^{+1} \longrightarrow Zn^{+2} + H_2$ — Cu^{+2}

Paramagnetism

Atoms, ions, and molecules with unpaired electrons are attracted to a magnet. This property s known as paramagnetism.

Any substance which is weakly attracted by a magnetic field is said to be **paramagnetic**, while if it is repelled it is **diamagnetic**. A substance in which all the electrons are paired are repelled by a magnet and are said to be diamagnetic.

Transition elements and their ions are generally paramagnetic, whereas most others are diamagnetic. The greater the number of unpaired electrons, the more paramagnetic is the ion.

Paramagnetism in transition elements is associated with unpaired electrons found in their partially filled d-orbitals, because there is a magnetic moment associated with the spinning electron. The magnetic moment rises with the number of unpaired electrons – and this gives a good indication of the number of unpaired electrons present in the atom / ion; maximum number of unpaired electrons in Mn^{+2} (5upe).

The metals, iron, cobalt and nickel are **ferromagnetic**, that is, they can exhibit magnetism in the absence of an external magnetic field.

Similar Physical and Chemical Properties

It should be no surprise to find similar chemical properties, because chemical reactions always involve the outer electrons, and the atoms in each transition series have the same outer most electron shell (4s, 5s, or 6s), nearly always containing two electrons.

Physical properties also depend on the outer electrons (especially metallic conductivity), and also on the way electron arrangement determines atomic radius. Similar atomic radius generally gives rise to similar physical properties.

The density of scandium: 3 g cm $^{-3}$ is much lower than of the other transition metals (mostly 7 - 8 g cm $^{-3}$), and the melting point of zinc : 420ºC is much lower than the melting point of the other transition metals (mostly above 1500ºC). Their anomolous physical properties provide another reason, in addition to the absence of partly filled d-orbitals in compounds, for excluding scandium and zinc from the transition metals.

Table of Properties of First Transition Series

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Metallic radius r_m/nm	0.145	0.132	0.137	0.137	0.124	0.125	0.125	0.128
Ionic radius (M^{2+}) r_m/nm	0.090	0.088	0.080	0.088	0.076	0.074	0.072	0.069
1st ionisation energy/kJ mol^{-1}	660	650	650	720	760	760	740	750
Electronegativity (Pauling)	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9

The general trends observed from the table above are:

there is a general decrease in radii, both metallic and ionic, from Ti to Cu. This is because the additional electrons are accommodated in the **same** sub-shell, which is drawn closer to the nucleus by the higher nuclear charge.

there is a general, though irregular, increase in first ionisation energy from Ti to Cu. The electron removed in ionisation, though always removed from the same sub-shell, is progressively more tightly bound because it is always partially shielded from the increasing nuclear charge.

there is a general small increase in electronegativity from Ti to Cu (ignoring the smaller value for Mn). This parallels the decrease in atomic radius.

[FYI: titanium is the ninth most abundant metal in the Earth's crust an was found in high percentage, (12%) in rocks brought back from the moon in Apollo. It is one of the metal most resistant to corrosion an has a low density. Titanium carbide is used in cutting tools, whilst titanium oxide, TiO_2 , commonly called rutile, is used extensively as a white pigment.]

How do the trends in radii, ionisation energy, and electronegativity for the elements in a short period (i) resemble and (ii) differ from the trends for transition elements.

The trends are in the same direction, i.e. radii decrease, while ionisation energies and electronegativities increase.

The range of the trends is very much greater for the short period elements than for the transition elements. For example, atomic radius varies from 0.124 nm (Fe) to 0.145 nm (Ti) in the transition elements, a difference of only 17% (i.e. not a very significant decrease in atomic radii). In period I, atomic radius varies from 0.060 nm (oxygen) to 0.152 nm (Li), a difference of 153% (i.e. a marked decrease).

In 'building up' the elements in a short period, e.g. from sodium to chlorine, the extra electrons are all added to the outer shell. The outer shell is not very effectively shielded from the increasing nuclear charge and is therefore drawn closer and closer to the nucleus, giving a considerable decrease in atomic radius across the period until a noble gas is formed..

However, in 'building up' the transition elements, the extra electrons are all added to an **inner** shell. The outer electrons which determine the radius of the atom are, therefore, more effectively shielded from the increased nuclear charge, so the decrease is less marked than in a short period.

The trends in ionisation energy and electronegativity are explained in the same way, since they depend largely on the atomic radius. The closer an electron is to the nucleus, the more energy is required to remove an electron from it (thus the higher the ionisation energy), and more readily will other electrons be attracted in covalent bonding (the higher the electronegativity).

High Density of Transition Elements

The densities of the transition elements are generally higher, (except for scandium), than the densities of the s-block metals which are generally low; especially Group I, e.g. copper is ~10 times as dense as potassium.

Densities of individual atoms increase markedly across a period because the atomic radii decrease while the atomic masses increase. Bulk densities increase similarly for the same packing arrangements.

The difference in densities between transition metals and Group I metals is accentuated by the fact that most transition metals have close-packed structures while Group I metals do not (i.e. a large number of atoms closely packed in a small space ∴ high densities and hard materials).

Atoms of most of the transition metals have small radii and pack in closest-packed structures with a coordination number of 12. They are .: relatively dense compared with the metals of Group IA and Group IIA whose larger atoms pack in body-centered structures with a coordination number of 8

High melting point and boiling point of Transition Elements

The melting point of transition metals are generally high (>1500ºC), except for zinc. The melting point of s-block are generally low, especially for Group I.

Melting point is an approximate indication of the strength of the bonding between particles. Strong bonding occurs in the transition metals where the atomic radius is small and the atomic structures are close-packed.

In the s-block metals metallic bonding is weaker because the atomic radius is larger. The difference is again most marked when comparing transition metals with Group I metals, which have the largest atomic radii and do not have close-packed structures. In addition, they have only one valency electron per atom to contribute to the 'sea of electrons'.

Boiling point of transition metals are generally high (~2000ºC), except for zinc again, compared to the s-block metals, which are generally low. This is for the same reason as for melting point, except boiling point is a better indication of bonding strength between particles, because vaporization separates the particles completely.

Enthalpies of fusion and vaporization show the same trend as mp and bp and are explained in a similar way.

Alloys

The similar atomic (and ionic) radii of the transition elements makes it possible for atoms (or ions) of one element to replace those of another element in the same solid structure. Thus, it is possible to make alloys containing transition elements in a wide range of composition. However, because the radii are not identical, some deformation of the structure occurs and it is this which modifies the physical properties.

Brass: Cu + Zn Cupronickel: Cu + NiSteel: Fe + Cr + V + Mo
Stainless: Fe + Cr + Ni

Interstitial Compounds

The transition metals consist of close-packed arrays of relatively large atoms. Between these atoms, in the 'holes' small atoms, such as H, B, C, N, can be inserted, without much distortion of the original structure to give interstitial compounds - the hydrides, borides, carbides, nitrides, e.g. TiC, Mn_4C, Fe_3N, TiH_2.

Because the metal structure is 'locked' by these small atoms, the resulting compound is often much harder than the original metal. Some of the compounds are .: of industrial importance - since these compounds are generally chemically inert, have higher m.pt., good conductivity and extremely hard. (In reality not all of the 'holes' are always filled).

Similarity in Chemical Properties

Transition elements generally:

- react with non-oxidising acids (e.g. dil. H_2SO_4, HCl), to give salts (usually metals in +2 oxidation state) and $H_{2(g)}$
- react with oxidising acids (conc. H_2SO_4, HNO_3) to give salts (sometimes higher oxidation state) and a gaseous reduction product of the acid (SO_2, or a mixture of oxides of nitrogen)
- react with oxygen, the halogens and sulphur, to give a variety of oxides, halides and sulphides.
- are not attacked by water, but react at higher temperatures with steam to give an oxide and $H_{2(g)}$
- have similar reactivities in the above reactions.

Colours of Hydrated 3d-Transition Metal Cations

In aqueous solutions, ions of the first -series elements (other than scandium and zinc— why?), form hydrates that impart characteristic colours to their solutions, see table below.

Formula of Hydrate	**Colour**
$[Ti(H_2O)_6]^{+3}$	violet
$[V(H_2O)_6]^{+3}$	green
$[Cr(H_2O)_6]^{+3}$	violet
$[Mn(H_2O)_6]^{+2}$	pale pink
$[Fe(H_2O)_6]^{+2}$	pale green
$[Fe(H_2O)_6]^{+3}$	yellow/orange
$[Co(H_2O)_6]^{+2}$	pink
$[Ni(H_2O)_6]^{+2}$	green
$[Cu(H_2O)_4]^{+2}$	blue

TRANSITION METALS : ASSIGNMENT

1.Write electron configurations for the following metals:
a) Ni b) Zr c) Cd^{+2} d) Ru^{+3} e) Mo^{+4}

2.Define each of the following:
a) ligand b) chelate c) bidentate d) complex ion

3.What must a ligand have in order to bond to a metal?

4.What do we mean when we say that a bond is a coordinate covalent bond?

5.Name the following coordinate compounds, and the complex ions:
a) $(Co(NH_3)_6)\ Cl_2$ b) $K_2(PtCl_4)$ c) $Ru(NH_3)_5Cl^{+2}$ d) $Fe(CN)_6^{\ -4}$

6.Why do transition metal ions often have several oxidation states, while other metals generally have one? Describe the maximum oxidation states observed along the series Sc – > Zn, identifying the element with the highest oxidation state and give the value of this state. What is the most common oxidation state of the elements Co – > Zn?

7.What is meant by a transition element? Summarize, with examples the distinctive properties of transition elements and show how they are related to the electronic structure of these elements.

8.This question concerns the d-block elements Sc – > Zn.
a)Describe the general electronic configuration of these elements and the exceptional configurations of chromium and copper.
b)Describe the bonding in these elements. Use a bonding model to account for the general increase in melting points from Sc (1540ºC) to Cr (1857ºC), followed by a general decrease to Cu (1083ºC) and Zn (420ºC).
c)Explain why the compounds of these elements are often coloured.

9.Iron is an important d-block element. Identify one physical property of iron that is similar to that of calcium and one that is different. Account for similarities and the differences on the atomic level. Give two ways in which the properties of the compounds of iron differ from those of calcium.

10. What colour would you expect a solution to appear if the solute absorbed light in the blue area of the spectrum.

11. Explain why V^{+3} is coloured and can act as a reducing agent, but Sc^{+3} is colourless and can not act as a reducing agent.

12. Two distinct compounds have the following formulas:
A: $[Cr(H_2O)_4Cl_2]Cl$ B: $Cr(H_2O)_4Cl_2$
Which of these two compounds is likely to have the:
(i) higher solubility (ii) higher melting point (iii) better conductivity in the liquid phase
Justify your answer in each case.

13. Explain why $Co(NH_3)_6^{\ +3}$ is not paramagnetic and $CoF_6^{\ -3}$ is.

14. Draw the structural formulas of cis– and trans– dichlorodiamminecobalt(II).

Further IB Exam Questions

1.This question concerns the atomic structure of iron.

(a) (i) Show the electron configurations (indicating electron spins) of iron and its positive ions, by filling in the boxes below: /3

	4s	3d				
Fe^0:						
Fe^{2+}:						
Fe^{3+}:						

(ii) What is the oxidation state of iron in $[Fe(CN)_6]^{4-}$?

/1

(iii) Iron can also exist in an oxidation state of +6. Give the formula of a species containing only iron and oxygen in which Fe(VI) might exist.

/1

(b) (i) Define the term *ligand.*

/1

(ii) In terms of acid-base theories, what type of a reaction is the formation of $[Fe(H_2O)_6]^{2+}$ from Fe^{2+} and water? Explain your answer.

/2

(iii) Explain why the two iron complex ions $[Fe(H_2O)_6]^{2+}$ and $[Fe(CN)_6]^{4-}$ are different colours.

/2

2. Iron shows the characteristic properties of a transition metal.

(a) Why does zinc not show the characteristic properties of a transition metal?

/1

(b) Give the electronic configuration of the Fe^{3+} ion.

/1

(c) Iron can form Fe^{2+} ions as well as Fe^{3+} ions. Give an example of another transition element that can show variable oxidation states, showing clearly **two** of its oxidation states.

/1

(d) Give the formula and describe the shape of the complex ion formed between Fe^{3+} and water.

/2

(e) Explain why complexes of Sc^{3+} are colourless whereas complexes containing Fe^{3+} are coloured. /2

(f) Explain why iron is used in the Haber process to manufacture ammonia and why is it added in finely divided form rather than in large pieces.

/2

3. (a) Define the term complex ion.

(b) Why are the transition metals able to form complexes?

(c) Why are these complexes coloured?

4. Name the following complex ions:

$[Cr(H_2O)_6]^{3+}$, $[Al(OH)_4]^-$, $[Cu(NH_3)_4]^{2+}$, $[CuCl_4]^{2-}$

5. State the oxidation number and the coordination number of the metal in each of these complexes:

(a)	$Ag(NH_3)_2 NO_3$	(e)	$[CuCl_4]^{-2}$
(b)	$Ni(CO)_4$	(f)	$[CuCl_4]^{-3}$
(c)	$K_3Fe(CN)_6$	(g)	$Zn(NH_3)_4SO_4$
(d)	$K_4Fe(CN)_6$	(h)	$[NiCl_4]^{-2}$

6. (a) What is meant by the terms ligand and complex ion? 2

(b) Give the full electronic configuration of the copper (II) ion. 1

(c) When anhydrous $CuCl_2$ is dissolved in water a blue solution results. Identify the species responsible for the blue colour and state the shape of this species. 2

(d) When anhydrous $CuCl_2$ is dissolved in concentrated $HCl_{(aq)}$, a yellow-green solution is formed due to the presence of the copper species **X**. If sulphur dioxide is bubbled through this yellow-green solution in the presence of an excess $HCl_{(aq)}$, the colourless species $[CuCl_2]^{-1}$ is formed together with SO_4^{-2} ions.

(i) Identify the yellow-green copper species, **X**, state its shape and give the oxidation state of copper in this species.

(ii) State the role of SO_2 in the conversion of species **X** into $[CuCl_2]^{-1}$.

(iii) Explain, in terms of electronic configuration, why $[CuCl_2]^{-1}$ is colourless.

(iv) When the solution containing the yellow-green copper species **X** is added to water, a blue solution is obtained. Write an ionic equation for this reaction. 6