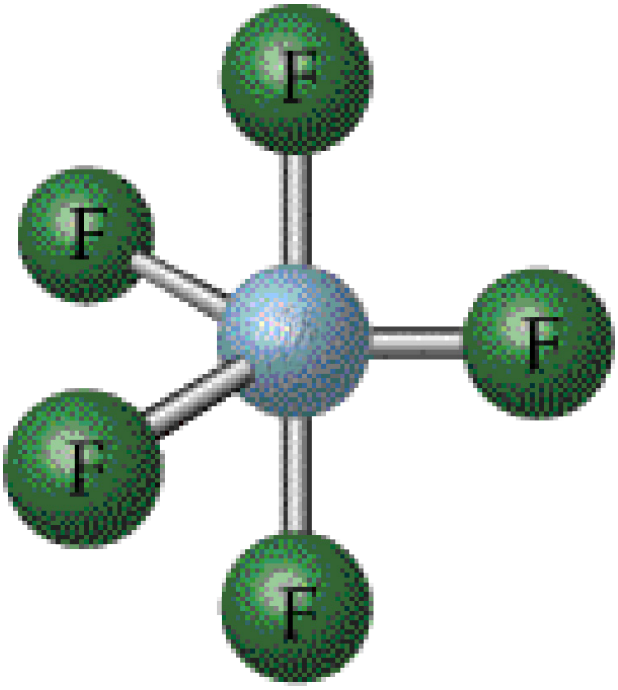
Unit 1 - Inorganic & Physical Chemistry

1.2 Bonding

Covalent Bonding
Shapes of Molecules & Polyatomic Ions
Transition Metal Chemistry



Learning Outcomes
Pupil Notes
Answers to Questions within Notes
Practice Questions
Answers to Practice Questions

Part 2.

Covalent Bonding

Non-polar covalent bonding and ionic bonding can be considered as being at opposite ends of a bonding continuum with polar covalent bonding lying between these two extremes

Different electron models can be used to explain the experimental evidence associated with covalent bonding

***Electron dot diagrams** represent bonding and non-bonding electron pairs in molecules and in polyatomic ions*

*A **dative covalent bond** is one in which one atom provides both electrons of the bonding pair*

Shapes of molecules and polyatomic ions

*The shapes of molecules or polyatomic ions can be predicted from the **number of bonding electron pairs** and the **number of non-bonding electron pairs***

*The arrangement of electron pairs is **linear**, **trigonal**, **tetrahedral**, **trigonal bipyramidal** and **octahedral** when the total number of electron pairs is 2, 3, 4, 5, and 6 respectively*

***Electron pair repulsions** decrease in strength in the order:*

non-bonding/non-bonding > non-bonding/bonding > bonding/bonding

*These different strengths of electron pair repulsion account for slight deviations from expected **bond angles** in molecules such as NH_3 and H_2O*

Electronic configuration of transition metals

*The d block transition metals are metals with an **incomplete d subshell** in at least one of their **ions***

*The filling of the d orbitals follows the Aufbau principle, with the exception of **chromium** and **copper** atoms. These exceptions are due to a special **stability** associated with all the d orbitals being **half filled** or **completely filled***

When transition metals form ions it is the s electrons which are lost first rather than the d electrons

Oxidation states of transition metals

An element is said to be in a particular oxidation state when it has a specific oxidation number

*The **oxidation number** is determined by following certain rules*

*Transition metals exhibit **variable oxidation states** of differing stability*

Compounds of the same transition metal, but in different oxidation states, may have different colours

Oxidation can be considered as an increase in oxidation number and reduction as a decrease in oxidation number

Compounds containing metals in high oxidation states tend to be oxidising agents, compounds with metals in low oxidation states are often reducing agents

Transition metal complexes

A complex consists of a central metal ion surrounded by ***ligands***

Ligands are ***electron donors*** *and may be negative ions or molecules with non-bonding pairs of electrons. Ligands can be classified as monodentate, bidentate etc*

The number of bonds from ligand(s) to the central metal ion is known as the ***coordination number*** *of the central ion*

Complexes are written and ***named*** *according to the IUPAC rules*

In a complex of a transition metal, the d orbitals are no longer degenerate. The degree of ***splitting*** *(loss of degeneracy) of the d orbitals depends on the position of the ligand in the spectrochemical series*

Colours *of many transition metal complexes can be* ***explained*** *in terms of d-d transitions.*

UV and visible spectroscopy

The effects of ***d—d transitions*** *can be studied using ultra-violet and visible absorption spectroscopy*

Ultra-violet and visible absorption spectroscopy involve transitions between electronic levels in atoms and molecules where the energy difference corresponds to the ultra-violet and visible regions of the electromagnetic spectrum

The wavelength ranges are approximately 200 - 400 nm for ultra-violet and 400-700 nm for visible

An ultra-violet/visible spectrometer measures the intensity of ***radiation transmitted*** *through the sample and compares this with the intensity of* ***incident radiation***

Catalysis

Transition metals or their compounds act as catalysts in many chemical reactions

It is believed that the presence of unpaired d electrons or unfilled d orbitals allows ***intermediate complexes*** *to form, providing reaction pathways of lower energy compared to the uncatalysed reaction*

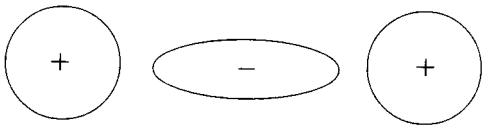
The ***variability of oxidation states*** *of transition metals is also an important factor*

PART 2

Atoms are held together in substances by chemical bonds and an understanding of chemical bonding is central to our understanding of chemistry, since the breaking and the forming of new bonds is basically what happens in chemical reactions. A chemical bond will form when atoms or molecules can rearrange their electrons in such a way as to bring about a new arrangement of electrons and nuclei of lower energy than before the bonding occurred.

A chemical bond can be considered to be the localisation of negative electrons holding together two adjacent positive nuclei (Figure 1).

Figure 1



A simple summary of bonding covered in Higher Chemistry is shown in Figure 17 where Δ*EN* = difference in electronegativity values between the two atoms forming the bond.

Figure 2

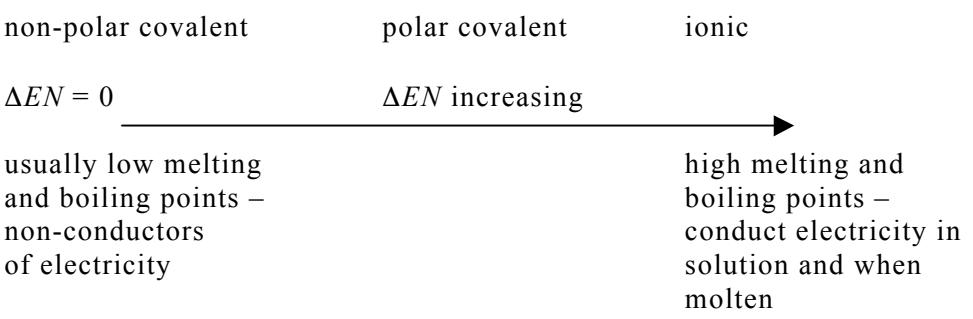


Figure 2 illustrates that non-polar covalent bonding and ionic bonding are considered as being at opposite ends of a bonding continuum with polar covalent bonding lying between these two extremes. This is very much a simplified summary with metallic bonding being ignored. There are also well-known exceptions such as carbon in the form of graphite, which can conduct electricity.

Electronegativity differences between atoms of different elements are helpful but do not always predict the type of bonding correctly. For example,

consider the two compounds sodium hydride (NaH) and water (H_2O):

sodium hydride: *EN* for Na = 0.9
EN for H = 2.2
so $\Delta EN = 2.2 - 0.9 = 1.3$

water: *EN* for H = 2.2
EN for O = 3.5
so $\Delta EN = 3.5 - 2.2 = 1.3$

It might therefore be expected that both compounds will have the same type of bonding, most likely polar covalent.

However, sodium hydride is a solid at room temperature and when melted and electrolysed, hydrogen gas is produced at the positive electrode. This demonstrates that sodium hydride is ionic and also that it contains the hydride ion, H^-. Water, of course, has polar covalent bonding.

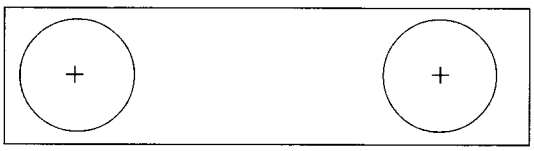
Electronegativity values and their differences are useful indicators of the type of bonding but it is also necessary to study the properties of the substance for confirmation or otherwise.

In general, ionic bonds involve metals from the left-hand side of the Periodic Table combining with non-metals from the far right-hand side. Covalent bonding usually occurs when the two bonding elements are non-metals that lie close to each other in the Periodic Table. Ignoring metallic bonding, most chemical bonds are somewhere between purely covalent and purely ionic.

Covalent bonding

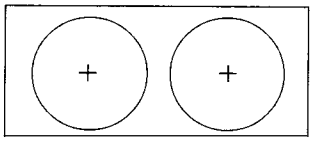
Consider what happens when two hydrogen atoms approach one another to form a hydrogen molecule. Each of the hydrogen atoms has a single proton in its nucleus and a single electron in the 1s orbital. These are shown separated in Figure 3.

Figure 3



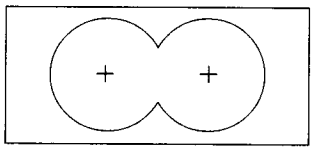
When the atoms move closer together (Figure 4) the electrostatic attraction between the nucleus of one atom and the electron of the other becomes significant and a drop in potential energy results.

Figure 4



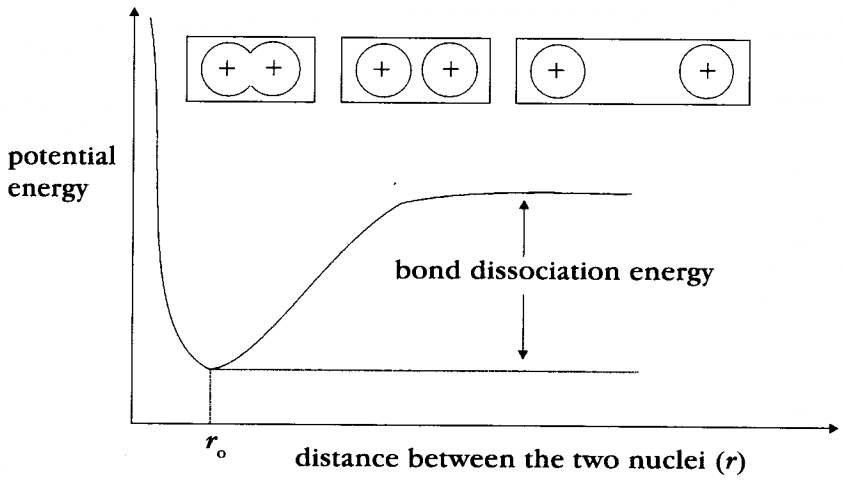
If the atoms become too close together, the repulsive force between the nuclei becomes more important and the potential energy increases again. The most stable situation, Figure 5, when the potential energy is at its lowest, is where the forces of attraction and repulsion balance.

Figure 5



Each atom now has a share of both electrons and there is a region of common electron density between the two nuclei. This electron density exerts an attractive force on each nucleus, keeping both atoms held tightly together in a covalent bond. Figure 6 shows the energy changes that occur when the orbitals from two hydrogen atoms overlap to form a covalent bond.

Figure 6



From Figure 6 it can be seen that in the formation of a covalent bond

- there is a merging or overlap of atomic orbitals
- the atoms take up position at a distance such that the forces of repulsion and attraction balance. This distance is known as the bond length (r_o).
- a certain amount of energy is released to the surroundings. This same amount of energy must be supplied to the molecule to break the bond. The energy required to break one mole of these bonds is known as the **bond enthalpy**, or bond dissociation energy.

A single covalent bond contains a shared pair of electrons. When two pairs of electrons are shared a double bond forms, as in oxygen (O=O). When three pairs of electrons are shared a triple bond forms, as in nitrogen (N≡N).

In 1916 the American chemist G N Lewis introduced the theory of the shared electron pair constituting a chemical bond. To honour his contribution electron-dot (or dot-and-cross) diagrams are known as Lewis electron-dot diagrams or simply Lewis diagrams.

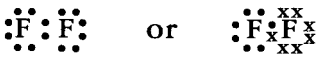
For example, the Lewis diagram for hydrogen is:

H:H

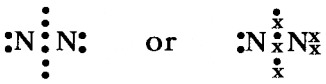
If we wish to show that each of the bonding electrons is from a different hydrogen atom the dot-and-cross variation can be used:

H x H

Similar diagrams for fluorine and nitrogen are:



and



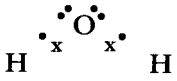
Question

Draw Lewis diagrams for

(a)	chlorine	(e)	hydrogen cyanide, HCN
(b)	hydrogen fluoride	(f)	methane
(c)	carbon dioxide	(g)	water
(d)	ammonia		

Some of the above questions contain pairs of electrons that are not involved in bonding. Such non-bonding pairs of electrons are often known as lone pairs.

For example, in water



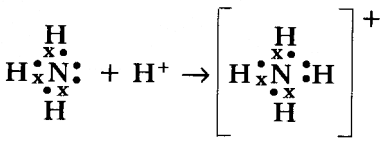
there are two bonding pairs of electrons ($\overset{\bullet}{\underset{x}{}}$)and two non-bonding pairs of electrons (:).

The total number of bonding and non-bonding pairs of electrons becomes important in determining the shapes of molecules (see page 29).

Sometimes both the electrons making up a covalent bond come from the same atom. This type of covalent bond is known as a **dative covalent bond** (or co-ordinate covalent bond). An example of the formation of a dative covalent bond is when ammonia gas is passed into a solution containing hydrogen ions to form the ammonium ion, NH_4^+:

$$NH_3(g) \quad + \quad H^+(aq) \quad \rightarrow \quad NH_4^+(aq)$$

The Lewis dot-and-cross diagram for this reaction is:



• = electron from nitrogen
x = electron from hydrogen

The hydrogen ion has no electrons and both electrons for the dative covalent bond come from the lone pair on the nitrogen atom. Once a dative covalent bond has formed it is the same as any other covalent bond. In the ammonium ion all four N–H bonds are identical.

Shapes of molecules and polyatomic ions

The shapes of molecules or polyatomic ions (e.g. NH_4^+) can be predicted from the number of bonding electron pairs and the number of non-bonding electron pairs (lone pairs). This is because the direction which covalent bonds take up in space is determined by the number of orbitals occupied by electron pairs and the repulsion between these orbitals. The repulsive effect of a non-bonded pair or lone pair of electrons is greater than that of a bonded pair and so the trend in repulsive effect is:

bonded pair:bonded pair < bonded pair:lone pair < lone pair:lone pair

The shape adopted by the molecule or polyatomic ion is the one in which the electron pairs in the outer shell get as far apart as possible. In other words, the shape in which there is the minimum repulsion between the electron pairs.

Consider some examples:

(a) **Two filled orbitals, both bonding pairs**, e.g. beryllium chloride, $BeCl_2(g)$

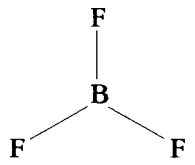
In the beryllium chloride molecule beryllium has two outer electrons and each chlorine atom contributes one electron and so there is a total of four electrons, i.e. two electron pairs, involved in bonding. These two bonding pairs will be as far apart as possible at 180° and so the beryllium chloride molecule is linear:

Cl—Be—Cl

(b) **Three filled orbitals, all bonding pairs**, e.g. boron trifluoride, BF_3

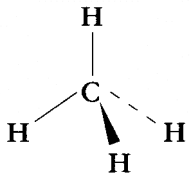
In the boron trifluoride molecule boron has three outer electrons and each fluoride atom contributes one electron to the structure. In total there are six electrons involved in bonding, resulting in three bonding pairs. Repulsions are minimised between these three bonding pairs when the molecule is flat and the bond angles are 120°. The name given

to this shape of molecule is trigonal planar (or simply trigonal):



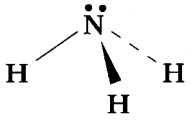
(c) **Four filled orbitals, all bonding pairs,** e.g. methane, CH_4

In methane, the central carbon atom has four outer electrons and each hydrogen atom contributes one electron to the structure and so there is a total of eight electrons involved in bonding, resulting in four electron pairs. The methane molecule is tetrahedral because this is the shape in which there is minimum repulsion between these electron pairs. The exact bond angles in methane are found using X-ray diffraction to be 109.5°, which is the true tetrahedral value:



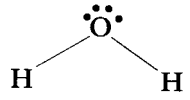
Four filled orbitals, three bonding pairs and one lone pair, e.g. ammonia, NH_3

In ammonia, the central nitrogen atom has five outer electrons and each hydrogen atom contributes one electron. There is a total of four electron pairs, but only three are bonding pairs, i.e. there are three N–H bonds while one pair of electrons is a non-bonding or lone pair. The arrangement of the electron pairs is tetrahedral but since there are only three bonds the shape is said to be pyramidal. There is greater repulsion between the lone pair and the three bonding pairs than there is between the three different bonding pairs with the result that the bonds are pushed closer together by the lone pair. Instead of a bond angle of 109.5°, the three bonds are angled at 107° to each other:

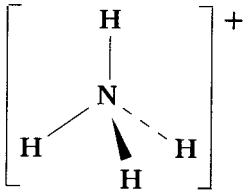


Four filled orbitals, two bonding pairs and two lone pairs, e.g. water, H_2O

In water, the central oxygen atom has six outer electrons and each hydrogen atom contributes one electron. There is a total of four electron pairs, but only two are bonding pairs. In other words, there are two O–H bonds and two non-bonding or lone pairs. The arrangement of the electron pairs is tetrahedral but since there is greater repulsion between the two lone pairs than between the lone pairs and the two bonding pairs the outcome is that the bonds are pushed even closer together in water than in ammonia. In water the bond angle is approximately 105° and the shape of the water molecule is bent:

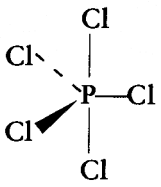


It is worth noting that if the lone pair on the nitrogen in ammonia were to form a dative covalent bond with a hydrogen ion to form the ammonium ion, there would be four equivalent bonding pairs and no non-bonding pairs. The shape of the ammonium ion would therefore be tetrahedral and all the bond angles would be 109.5°, as in methane:



(d) Five filled orbitals, all bonding pairs, e.g. gaseous phosphorus(V) chloride, $PCl_5(g)$

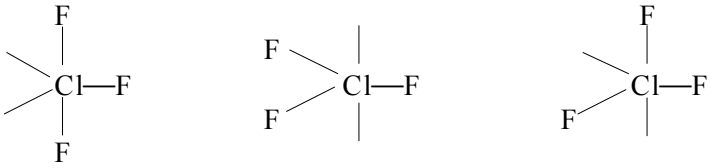
In gaseous phosphorus(V) chloride the central phosphorus atom has five outer electrons and each chlorine atom contributes one electron to make five electron pairs. There will be no lone pairs as there will be five P–Cl bonds. The shape of the molecule is trigonal bipyramidal:



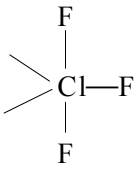
With no lone pairs on the central phosphorus atom, the bond angles between the three central chlorine atoms are 120°. The upper chlorine atom has bond angles of 90° to the three central chlorine atoms as does the lower chlorine atom. The bond angle between the upper and lower chlorine atom is 180°.

Five filled orbitals, three bonding pairs and two lone pairs, e.g. chlorine(III) fluoride, ClF_3

In chlorine(III) fluoride the central chlorine atom has seven outer electrons and each fluorine atom contributes one electron to make five electron pairs in total. Three of these will be bonding pairs and two will be lone pairs. The five electron pairs will be in a trigonal bipyramidal arrangement but the actual shape of the molecule depends on the arrangement of the bonds. There are three possible options (showing all electron pairs as solid lines in this case):



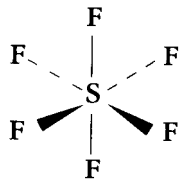
Considering all the repulsive forces between the electron pairs and taking into account that there is greatest repulsion at 90° and least at 180°, and also remembering that the trend in repulsive effect is bonded pair:bonded pair < bonded pair:lone pair < lone pair:lone pair, the most stable option is:



The ClF_3 molecule is said to be 'T-shaped'.

(e) **Six filled orbitals, all bonding pairs**, e.g. sulphur hexafluoride, SF_6

In sulphur hexafluoride, the central sulphur atom has six outer electrons and each fluorine atom contributes one electron, resulting in six electron pairs, all of which are bonding pairs. The shape of the molecule is:



If this molecule were constructed in a solid shape it would be a regular octahedron and therefore the SF_6 molecule is octahedral in shape.

Bearing in mind that the number of electron pairs decides the shape of molecules, Table 1 provides a useful summary of molecular shapes.

Table 1

Total number of electron pairs	**Arrangement of electron pairs**
2	Linear
3	Trigonal
4	Tetrahedral
5	Trigonal bipyramidal
6	Octahedral

Question

Draw molecules of the following species showing their shapes:

(a) PCl_3 (d) PF_5 (g) NF_3

(b) $SnCl_4$ (e) BeF_2 (h) BH_4^-

(c) BrF_4^- (f) H_2S

Electronic configuration and oxidation states of the transition metals

Electronic configuration

The d-block transition metals are defined as metals with an incomplete d subshell in at least one of their ions. When a transition metal atom loses electrons to form a positive ion the 4s electrons are lost before the electrons occupying the 3d orbitals.

Consider the electronic configurations of the transition elements using [Ar] to represent that of argon [$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$] (Table 19).

Table 2

	Electronic configuration	
Element	**Spectroscopic notation**	**Orbital box notation (d electrons only)**
Scandium	[Ar] $3d^1$ $4s^2$	↑ ☐ ☐ ☐ ☐
Titanium	[Ar] $3d^2$ $4s^2$	↑ ↑ ☐ ☐ ☐
Vanadium	[Ar] $3d^3$ $4s^2$	↑ ↑ ↑ ☐ ☐
Chromium	[Ar] $3d^5$ $4s^1$	↑ ↑ ↑ ↑ ↑
Manganese	[Ar] $3d^5$ $4s^2$	↑ ↑ ↑ ↑ ↑
Iron	[Ar] $3d^6$ $4s^2$	↑↓ ↑ ↑ ↑ ↑
Cobalt	[Ar] $3d^7$ $4s^2$	↑↓ ↑↓ ↑ ↑ ↑
Nickel	[Ar] $3d^8$ $4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑
Copper	[Ar] $3d^{10}$ $4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Zinc	[Ar] $3d^{10}$ $4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

As can be seen from Table 2, the filling of the d orbitals follows the aufbau principle, with the exception of chromium and copper atoms. These exceptions are due to a special stability associated with all the d orbitals being half filled, as in the case of chromium, or completely filled, as in the

case of copper. This is better seen using the orbital box notation.

When transition metals form positive ions it is the s electrons that are lost first rather than the d electrons, e.g. the electronic configuration for an iron atom is [Ar] $3d^6$ $4s^2$ and so the electronic configuration for the iron(II) ion will be [Ar] $3d^6$.

Questions

1. Write down the electronic configurations in both spectroscopic and orbital box notation for the following atoms and ions.
   (a) Cu
   (b) Mn^{2+}
   (c) Ti^{3+}
   (d) Co
   (e) Co^{2+}
   (f) Co^{3+}
   (g) Ni^{2+}
   (h) Cu^{+}
   (i) Fe^{3+}

2. Zinc invariably forms the 2+ ion and the only ion of scandium is the 3+ ion. Using spectroscopic notation, write down the electronic configurations for both these ions and use them to explain why zinc and scandium are often regarded as not being transition metals.

Oxidation states

In ionic compounds the oxidation number is equal to the charge on the ion in a compound. For example, in iron(II) chloride, $Fe^{2+}(Cl^{-})_2$, iron is in oxidation state +2 and in iron(III) chloride, $Fe^{3+}(Cl^{-})_3$, iron is in oxidation state +3. The two terms, oxidation state and oxidation number, are usually interchangeable and so an element is said to be in a particular oxidation state when it has a specific oxidation number.

There are certain rules for assigning and using oxidation numbers. These are:

1. The oxidation number in a free or uncombined element is zero. Thus, metallic magnesium has an oxidation number of zero as does Cl in chlorine gas, Cl_2.

2. For ions consisting of single atoms the oxidation number is the same as the charge on the ion. For example, the oxidation number of chlorine in Cl^- is –1, for oxygen in O^{2-} it is –2 and for aluminium in Al^{3+} it is +3.
3. In **most** compounds the oxidation number for hydrogen is +1 and for oxygen it is –2. Notable exceptions are metallic hydrides (–1 for hydrogen) and peroxides (–1 for oxygen).
4. In its compounds fluorine always has oxidation number –1.
5. The algebraic sum of all the oxidation numbers in a molecule must be equal to zero.
6. The algebraic sum of all the oxidation numbers in a polyatomic ion must be equal to the charge on the ion. For example, in SO_4^{2-} the sum of the oxidation numbers of the one sulphur and four oxygen atoms must equal –2.

Question

Use the rules above to find the oxidation numbers of:
(a) Mn in MnF_2
(b) S in SO_2
(c) S in SO_3
(d) C in CO_3^{2-}
(e) Mn in MnO_2
(f) S in SO_4^{2-}
(g) Mn in MnO_4^{2-}
(h) Mn in MnO_4^-
(i) Cu in $CuCl_4^{2-}$

Oxidation numbers can be used to determine whether an oxidation–reduction reaction has taken place. **An increase in oxidation number means that oxidation of the species has occurred, whereas a decrease in oxidation number means that reduction has occurred.**

For example, consider the oxidation number of manganese as it changes from MnO_4^- to Mn^{2+}. The oxidation number of manganese in MnO_4^- is +7, but in Mn^{2+} manganese is in oxidation state +2. This means that when MnO_4^- is changed to Mn^{2+} a reduction reaction has taken place. This fits in with the more familiar definition that reduction is a gain of electrons, as shown in the ion–electron equation:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

It can be seen that manganese in oxidation state +7 has been reduced and so MnO_4^- is acting as an oxidising agent when it reacts in such a manner. It is

generally true that compounds containing metals in high oxidation states tend to be oxidising agents whereas compounds with metals in low oxidation states are often reducing agents.

Questions

1. Write an ion–electron equation for Fe^{2+} acting as:
   (i) an oxidising agent
   (ii) a reducing agent.

2. Work out the oxidation number of Cr in $Cr_2O_7^{2-}$ and decide whether the conversion of $Cr_2O_7^{2-}$ to Cr^{3+} is oxidation or reduction. Is the $Cr_2O_7^{2-}$ acting as an oxidising agent or a reducing agent in this reaction? Confirm your answer by writing the appropriate ion–electron equation.

3. Work out the oxidation number of chromium in $Cr_2O_7^{2-}$ and in CrO_4^{2-} and decide whether the conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-} is oxidation or reduction.

4. The most common oxidation states of iron are +2 and +3. Using orbital box notation, draw out their respective electronic configurations and suggest which of the two ions is the more stable.

Transition metals exhibit variable oxidation states of differing stability. A common oxidation state of most of these elements is +2 when the atom has lost its 4s electrons. However, because the 3d subshells have energy levels very close to that of the 4s subshell, it is fairly easy for the 3d electrons to be also lost to form other oxidation states. The different ions in different oxidation states have different stabilities, as in the case of Fe^{2+} and Fe^{3+} (see question 4 above). Changing from one oxidation state to another is an important aspect of transition metal chemistry, often characterised by a distinct colour change, as shown in Table 3.

Table 3

Ion	Oxidation state of transition metal	Colour
VO_3^-	+5	Yellow
VO^{2+}	+4	Blue
V^{3+}	+3	Green
V^{2+}	+2	Violet

The multiplicity of different oxidation states shown by some transition metals is given in Table 4. The most stable oxidation states are in bold type.

Table 4

Element	Different oxidation states	Examples of compounds
Ti	+2, **+3**, **+4**	Ti_2O_3, TiO_2
V	+1, +2, **+3**, **+4**, **+5**	VCl_3, V_2O_5
Cr	+1, +2, **+3**, +4, +5, **+6**	Cr_2O_3, CrO_3
Mn	+1, **+2**, +3, **+4**, +5, +6, **+7**	$MnCl_2$, MnO_2
Fe	+1, **+2**, **+3**, +4, +6	$FeCl_2$, Fe_2O_3
Co	+1, **+2**, **+3**, +4, +5	CoO, $CoCl_3$
Ni	+1, **+2**, +3, +4	NiO, $NiCl_2$
Cu	+**1**, **+2**, +3	Cu_2O, $CuCl_2$

Question

Suggest why scandium and zinc are not included in Table 4.

Transition metal complexes

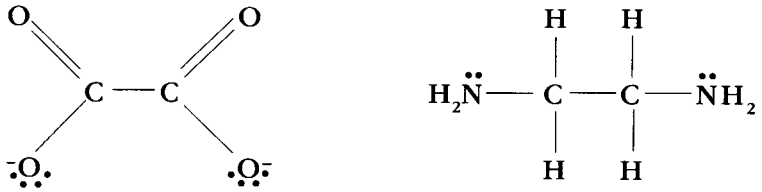
A complex consists of a central metal ion surrounded by **ligands**. A ligand is a molecule or negative ion which bonds to the metal ion by the donation of one or more electron pairs into unfilled metal orbitals.

The most common neutral compound to act as a ligand is water, which bonds to the central metal ion through one of the lone pairs on the oxygen atom. Ammonia, NH_3, is also a neutral ligand, bonding through the lone pair on the nitrogen atom.

Common ligands that are negative ions include:
- cyanide ion, CN^-
- halides, F^-, Cl^-, Br^- and I^-
- nitrite ion, NO_2^-
- hydroxide ion, OH^-.

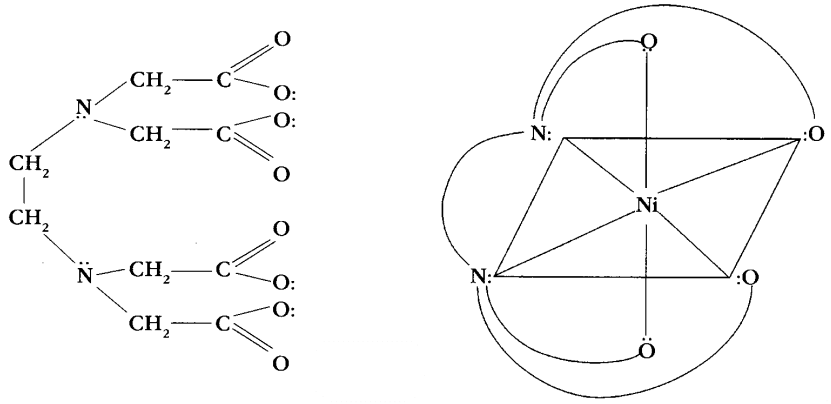
Ligands such as CN^-, H_2O, NH_3 and other molecules or negative ions donating one electron pair to the metal ion are said to be **monodentate**. Those that donate more than one electron pair are polydentate. The term 'dentate' is derived from the Latin word for tooth and so monodentate ligands can be considered as one-toothed ligands. Ligands are also said to be chelating, from the Greek word meaning a claw. If the ligand has two lone pairs, it is called a **bidentate** chelate. Common bidentate ligands are the ethanedioate (oxalate) ion and 1,2-diaminoethane (ethylenediamine), both of which are shown in Figure 7.

Figure 7



A common reagent in volumetric analysis is EDTA, ethylenediaminetetraacetic acid. It is a **hexadentate** ligand which complexes with many metals in a 1:1 ratio (Figure 8).

Figure 8: *(a) Structure of EDTA; (b) complex of EDTA with nickel*



The number of ligands in a complex ion varies depending on the particular ligand. For example, in $[Cu(H_2O)_6]^{2+}$ the copper(II) ion is surrounded by six water molecules and in $[CuCl_4]^{2-}$ there are four chloride ions acting as ligands around the copper(II) ion. The number of bonds from the ligand to the central metal ion is known as the **co-ordination number** of the central ion and in the two examples given above the copper(II) ion has co-ordination numbers 6 and 4 respectively.

Naming complex ions

Complex ions and complexes are written and named according to IUPAC rules.

The formula of a complex ion should be enclosed within square brackets, although common complexes such as MnO_4^- are often written without brackets. The metal symbol is written first, then the negative ligands followed by the neutral ligands, e.g. $[Fe(OH)_2(H_2O)_4]^+$.

When naming the complex ion or molecule the ligands should be named first, in alphabetical order, followed by the name of the metal.
If the ligand is a negative ion the name of which ends in -ide, the ending changes to 'o', e.g. chloride, Cl^-, becomes chloro, cyanide, CN^-, becomes cyano.

If the ligand is a negative ion the name of which ends in -ite, the final 'e' changes to 'o', e.g. nitrite, NO_2^-, changes to nitrito.

If the ligand is water it is named aqua, ammonia is named ammine and carbon monoxide is carbonyl.

If there is more than one particular ligand it is prefixed by di, tri, tetra, penta, or hexa, etc. as appropriate.

If the complex ion is an anion (negative ion) the suffix -ate is added to the name of the metal. Sometimes the Latin name for the metal is used in this context, e.g. ferrate not ironate and cuprate rather than copperate.

The oxidation state of the metal is given in Roman numerals after its name.

For example, the complex ion $[Ni(NH_3)_6]^{2+}$ is named hexaamminenickel(II) and the negative complex ion $[Fe(CN)_6]^{3-}$ is named hexacyanoferrate(III).

Question

Name the following complexes:

(a) $[CoCl_4]^{2-}$
(b) $[Ni(H_2O)_6]^{2+}$
(c) $[Fe(CN)_6]^{4-}$
(d) $[Ti(NH_3)_6]^{3+}$
(e) $[Ni(CN)_6]^{4-}$
(f) MnO_4^-
(g) $[PtCl_6]^{2-}$
(h) $Ni(CO)_4$
(i) $[Cu(NH_3)_4]^{2+}$

Simple ions and complex ions of the transition metals are often coloured. This is because they **absorb** light in certain parts of the visible spectrum. The colour seen is the complementary colour to that absorbed, i.e. it is a combination of the colours not absorbed.
To understand this outcome, it has to be appreciated that white light is a combination of the three primary colours red, blue and green.

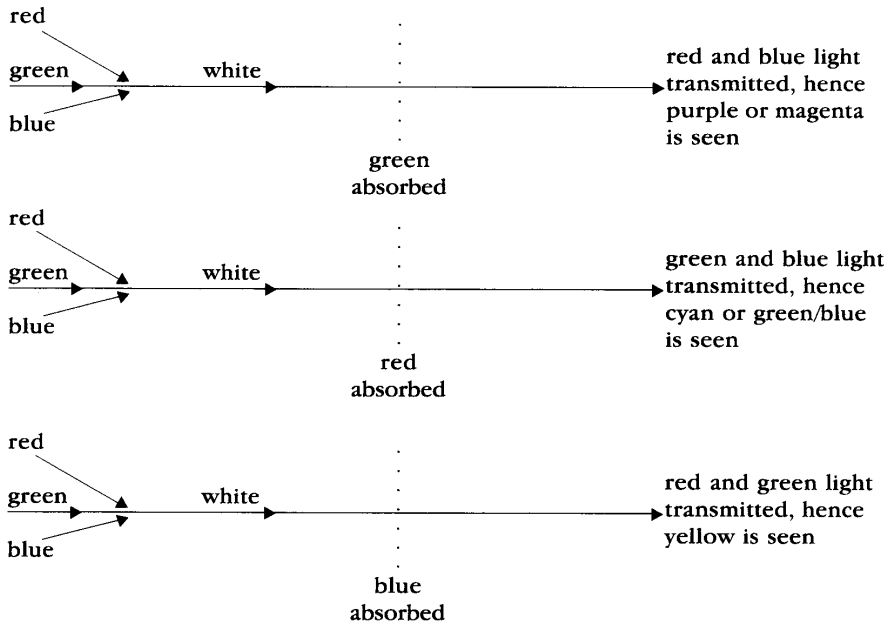
If red light is absorbed, the colours transmitted are blue and green, which is seen as green/blue or cyan.

If blue light is absorbed, the colours transmitted are red and green, which is seen as yellow.

If green light is absorbed the colours transmitted are blue and red, which is seen as magenta.

These colour changes are summarised in Figure 9.

Figure 9



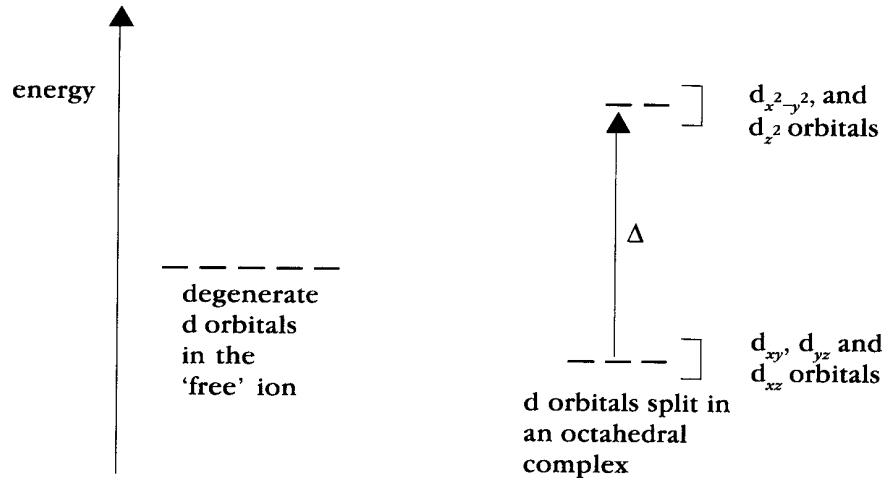
The reason that compounds of transition metals absorb white light is the loss of degeneracy of the d orbitals in these compounds. In the free ion, the five different 3d orbitals (d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}) are degenerate, i.e. of equal energy. However, in a complex such as $[Ti(H_2O)_6]^{3+}$ the metal ion is no longer isolated but is surrounded by the six water molecules serving as ligands. The complex has an octahedral shape and the water molecules can be considered to approach the central Ti^{3+} along the *x*-, *y*- and *z*-axes.

Due to electrostatic repulsion, the orbitals that lie on these axes will be raised to higher energy than those orbitals that lie between the axes.

The d_{xy}, d_{yz} and d_{xz} orbitals lie between the axes. For example, the d_{xy} orbital lies between the *x*- and *y*-axes and so on. The $d_{x^2-y^2}$ orbital has a double dumb-bell shape with the lobes lying along the *x*- and *y*-axes. The d_{z^2} orbital has both its large lobes lying along the *z*-axis.

This results in the $d_{x^2-y^2}$ and d_{z^2} orbitals being of higher energy than the d_{xy}, d_{yz} and d_{xz} orbitals in the octahedral complex. This is shown diagrammatically in Figure 10.

Figure 10



The d orbitals are split differently in complexes of different shapes. The amount of splitting, Δ, of the d orbitals depends on the ligand. The ability of ligands to cause the splitting of the d orbitals is given by the **spectrochemical** series. For the most common ligands this is:

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < CN^-$

small orbital splitting — large orbital splitting
'weak' field ligands — 'strong' field ligands

Transition metal complexes can absorb light because photons of the appropriate energy can excite electrons from the d orbitals of lower energy (ground state) to d orbitals of higher energy (excited state). This energy is dissipated as heat and is not re-emitted as light.

For example, consider the $Cu^{2+}(aq)$ ion. It has electronic configuration [Ar] $3d^9$ and this is shown diagrammatically in Figure 39 in which an electron is represented by an arrow.

Figure 11

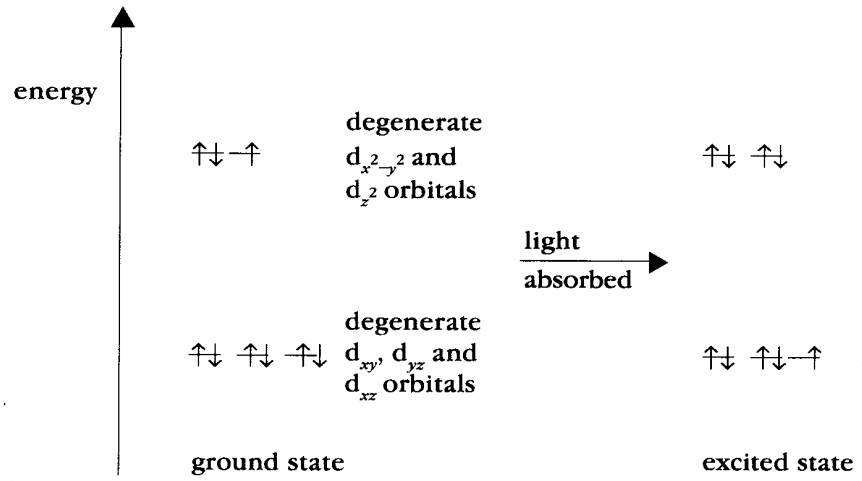


Figure 11 shows an electron from one of the lower energy orbitals being promoted to a higher energy orbital. This transition is known as a **d–d transition**. If the energy absorbed corresponds to the visible part of the electromagnetic spectrum, then the colour observed will be the complementary colour to that absorbed. In the case of Cu^{2+}, red light is absorbed, giving the familiar blue-green colour of copper(II) ions in aqueous solution. Changing the ligand can change this colour. For example, replacing the water molecules by chloride ions (by adding concentrated HCl) produces a green colour, and a dark blue or violet colour is observed when the water molecules are replaced by ammonia molecules as ligands.

The colours of many transition metal complexes can be explained in terms of d–d transitions, but only if there are electrons in the d orbitals to begin with. For example, the intense purple colour of permanganate ions (MnO_4^-) cannot be explained by d–d transitions as Mn is in oxidation state +7 with an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Because there are no d electrons available another explanation apart from d–d transitions has to be used to explain the colour. This other type of transition is known as 'charge-transfer' transition but this is outside the scope of Advanced Higher Chemistry.

Ultra-violet and visible absorption spectroscopy

The effects of d–d transitions can be studied using ultra-violet and visible absorption spectroscopy. The absorption of ultra-violet or visible radiation corresponds to outer electrons becoming excited. When an atom, molecule or

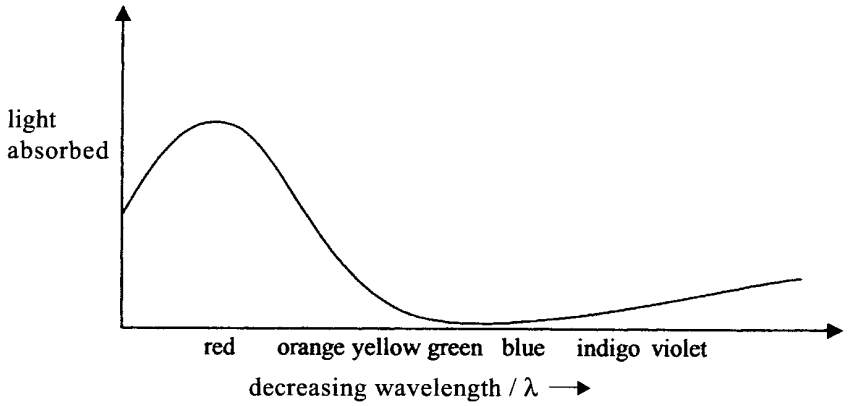
ion absorbs energy, electrons are promoted from their ground state to an excited state. The energy difference between these states corresponds to the ultra-violet and visible regions of the electromagnetic spectrum. For ultra-violet radiation the wavelength range is approximately 200–400 nm and for visible radiation the wavelength radiation is approximately 400–700 nm. Since ultra-violet radiation has shorter wavelengths it is of higher energy than visible radiation.

Most transition metal compounds are coloured because they absorb visible radiation. Solutions that absorb ultra-violet but not visible radiation appear colourless, as our eyes are unable to detect that ultra-violet radiation has been removed from the transmitted light.

An ultra-violet/visible absorption spectrophotometer contains a source and a detector of ultra-violet and/or visible radiation. The radiation from the source is focused into a beam and passes through a diffraction grating, which splits it into its constituent wavelengths. In some instruments the radiation is also split into two separate beams, one beam passing through a solution of the sample being investigated and the other passing through a reference cell, which usually contains the solvent only. As the radiation passes through the sample, photons of a specific frequency, corresponding to the energy difference between the ground state and the excited state to which the electron is promoted, are absorbed. The radiation of this particular frequency is absorbed so the transmitted radiation emerges from the sample with a decreased intensity. If photons of a given frequency are not absorbed then radiation corresponding to this frequency is unchanged as it passes through the sample. The spectrometer measures the intensity of the radiation transmitted through the sample and compares this value with the intensity of the incident radiation. The instrument usually plots the intensity of light absorbed at a particular frequency or wavelength against the frequency or wavelength of the radiation. The outcome is known as the absorption spectrum of that sample. When there is absorption of radiation in a certain frequency range, the spectrum shows an absorption band. In the case of visible light being absorbed, the colour transmitted is white light minus the absorbed light and the complementary colour is observed.

For example, the blue $[Cu(H_2O)_6]^{2+}$ ion, which is present in aqueous solutions of copper(II) sulphate, copper(II) chloride, etc., has an absorption band in the red part of the visible spectrum, as shown in Figure 12. Since red light is absorbed, blue and green light are transmitted and aqueous copper(II) salts appear blue-green (cyan) to our eyes.

Figure 12



For the complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$ the absorption band is moved slightly more towards green so that both red and green light are absorbed and solutions containing this ion are darker blue in colour.

Catalysis

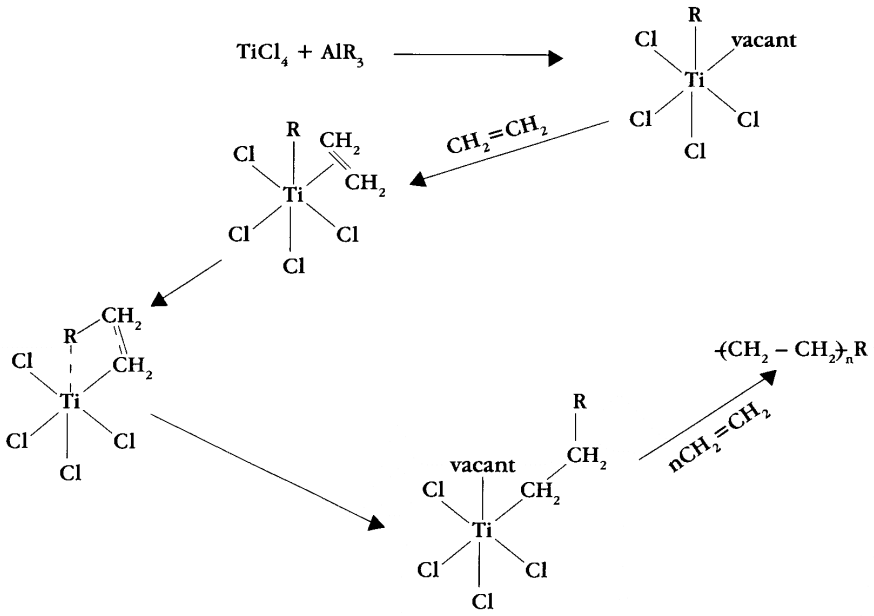
Transition metals and their compounds act as catalysts in many important industrial chemical reactions, some of which are summarised in Table 5.

Table 5

Process	**Catalyst used**
Haber	Iron granules
Contact	Vanadium(V) oxide
Ostwald	Platinum gauze
Catalytic converters in cars	Platinum, palladium and rhodium
Preparation of methanol	Copper
Preparation of margarine	Nickel
Polymerisation of alkenes	Titanium compounds

Catalysts speed up chemical reactions by providing an alternative reaction pathway of lower activation energy. Transition metals can form a variable number of bonds because of the availability of unoccupied or partially occupied d orbitals. It is believed that the presence of unpaired electrons or unfilled d orbitals allows intermediate complexes to form, providing reaction pathways of lower energy compared to the uncatalysed reaction. Transition metals usually have co-ordination numbers of 4, 5 or 6 in their complexes and this allows reactant species to attach themselves to the transition metal in a compound in which the co-ordination number of the transition metal is 4. The catalysed reaction can then take place without disturbing the other ligands although the size and shape of these can direct the course of the reaction. The product formed leaves the catalyst, and the catalyst is left unchanged at the end of the reaction. For example, passing ethene into a solution containing $TiCl_4$ and $(C_2H_5)_3Al$ causes its polymerisation into poly(ethene). Figure 13, in which 'R' represents the ethyl groups, shows how the co-ordination number of Ti changes as it catalyses the reaction. Catalysts like this are known as Ziegler-Natta catalysts and they allow polymers with particular desirable properties to be tailor-made at low temperatures and pressures. Ziegler and Natta were jointly awarded the Nobel Prize for Chemistry in 1963 for their contribution to polymer chemistry.

Figure 13



Many transition metals act as catalysts because of their ability to exist in a variety of different oxidation states. This also allows the transition metal to provide an alternative reaction pathway with lower activation energy and so speed up the reaction. The transition metal reverts to its original oxidation state once the reaction is complete.

A good example occurs on adding pink cobalt(II) chloride solution to a solution of hydrogen peroxide and Rochelle salt (potassium sodium tartrate) at about 50°C. Before the cobalt(II) ions are added the reaction progresses very slowly with only a few bubbles of gas being released. Almost immediately on adding the $CoCl_2(aq)$ there is a colour change from pink to green and vigorous effervescence. When the reaction is over the pink colour returns. In terms of oxidation states the cobalt has changed from +2 (pink) to +3 (green) and then back to +2 at the end:

$Co^{2+}(aq)$	→	$Co^{3+}(aq)$	→	$Co^{2+}(aq)$
pink		green		pink

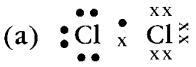
Page 4

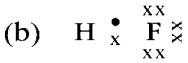
Question

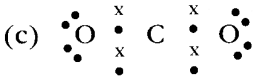
Draw Lewis diagrams for

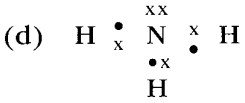
(a) chlorine
(b) hydrogen fluoride
(c) carbon dioxide
(d) ammonia
(e) hydrogen cyanide, HCN
(f) methane
(g) water

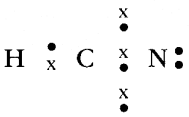
Answers

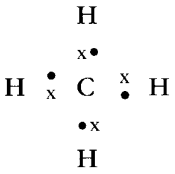
(a) 

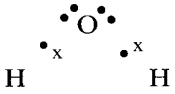
(b) 

(c) 

(d) 

(e) 

(f) 

(g) 

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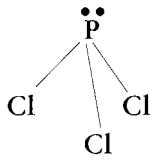
Question

Draw molecules of the following species showing their shape.

(a) PCl_3
(b) $SnCl_4$
(c) BrF_4^-
(d) PF_5
(e) BeF_2
(f) H_2S
(g) NF_3
(h) BH_4^-

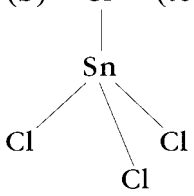
Answers

(a)  (pyramidal)

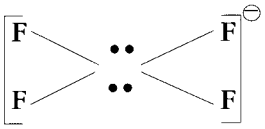
In PCl_3 there are four electron pairs arranged tetrahedrally around the phosphorus atom. Three of the electron pairs are bonding pairs and there is one non-bonding pair of electrons giving the molecule a pyramidal shape.

In $SnCl_4$ there are four electron pairs around the tin atom. These electron pairs are all bonding pairs and so the molecular shape is tetrahedral

(b) Cl (tetrahedral)

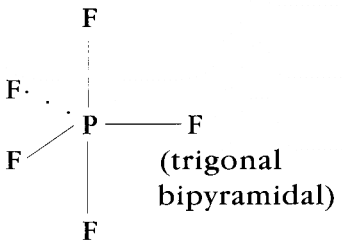


(c)



In BrF_4^- there are six electron pairs arranged octahedrally around the central bromine atom. Four of these electron pairs are bonding pairs and the other two are non-bonding pairs. Since the two non-bonding pairs will be above and below the plane to minimise their repulsive effects, the bonds will be arranged as shown opposite and the ion has a square planar shape.

(d)



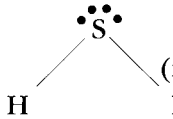
(trigonal bipyramidal)

In PF_5 there are five electron pairs around the central phosphorus atom. All five electron pairs are bonding pairs and are arranged as shown, and the shape of the molecule is trigonal bipyramidal.

(e) F—Be—F (linear)

In BeF_2 both electron pairs are bonding pairs and are arranged at 180° around the central beryllium atom.

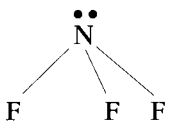
(f)



(non-linear or bent)

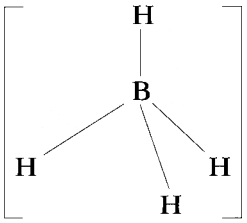
In H_2S there are four electron pairs arranged tetrahedrally around the central sulphur atom. The two bonding pairs are arranged as shown and the molecule is non-linear.

(g)



(pyramidal)

In NF_3 the four electron pairs are arranged tetrahedrally around the central nitrogen atom. The three bonding pairs are arranged as shown and the molecule is pyramidal in shape

(h) 

⊖ (tetrahedral)

In BH_4^- there are four pairs of electrons arranged tetrahedrally around the central boron atom. Each electron pair is a bonding pair and so the ion has a tetrahedral shape.

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Question 1 (with answers shown)

Write down the electronic configurations in both spectroscopic and orbital box notation for the following atoms and ions.

	Electronic configuration	
Species	spectroscopic notation	orbital box notation (d electrons only)
(a) Cu	$[Ar]3d^{10}4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
(b) Mn^{2+}	$[Ar]3d^5$	↑ ↑ ↑ ↑ ↑
(c) Ti^{3+}	$[Ar]3d^1$	↑
(d) Co	$[Ar]3d^74s^2$	↑↓ ↑↓ ↑ ↑ ↑
(e) Co^{2+}	$[Ar]3d^7$	↑↓ ↑↓ ↑ ↑ ↑
(f) Co^{3+}	$[Ar]3d^6$	↑↓ ↑ ↑ ↑ ↑
(g) Ni^{2+}	$[Ar]3d^8$	↑↓ ↑↓ ↑↓ ↑ ↑
(h) Cu^+	$[Ar]3d^{10}$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
(i) Fe^{3+}	$[Ar]3d^5$	↑ ↑ ↑ ↑ ↑

Question 2

Zinc invariably forms the 2+ ion and the only ion of scandium is the 3+ ion. Using spectroscopic notation, write down the electronic configurations for both these ions and use them to explain why zinc and scandium are often regarded as not being transition metals.

Answers

Zn^{2+} $[Ar]3d^{10}$ Sc^{3+} $[Ar]$

Transition metals are often defined as metals that have an incomplete d subshell in at least one of their ions. Since ions of zinc and scandium do not have an incomplete d subshell, they are often regarded as not being transition metals.

Page 13

Questions (with answers alongside)

Use the rules on pages 12–13 to find the oxidation numbers of:

(a) Mn in MnF_2 (+2)

(b) S in SO_2 (+4)

(c) S in SO_3 (+6)

(d) C in CO_3^{2-} (+4)

(e) Mn in MnO_2 (+4)

(f) S in SO_4^{2-} (+6)

(g) Mn in MnO_4^{2-} (+6)

(h) Mn in MnO_4^{-} (+7)

(i) Cu in $CuCl_4^{2-}$ (+2)

Page 14

Question 1

Write an ion electron equation for Fe^{2+} acting as:
(i) an oxidising agent (ii) a reducing agent.

Answers

(i) $Fe^{2+} + 2e^- \rightarrow Fe$ (ii) $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Question 2

Work out the oxidation number of Cr in $Cr_2O_7^{2-}$ and decide whether the conversion of $Cr_2O_7^{2-}$ to Cr^{3+} is oxidation or reduction. Is the $Cr_2O_7^{2-}$ acting as an oxidising agent or a reducing agent in this reaction? Confirm your answer by writing the appropriate ion–electron equation.

Answer

In $Cr_2O_7^{2-}$, Cr has oxidation number +6 and so the conversion of $Cr_2O_7^{2-}$ to Cr^{3+} is reduction since there is a decrease in oxidation number. The $Cr_2O_7^{2-}$ is acting as an oxidising agent. The appropriate ion–electron equation is

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

Question 3

Work out the oxidation number of chromium in $Cr_2O_7^{2-}$ and in CrO_4^{2-} and decide whether the conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-} is oxidation or reduction.

Answer

Since the oxidation number of chromium in both $Cr_2O_7^{2-}$ and CrO_4^{2-} is +6 then the conversion of $Cr_2O_7^{2-}$ to CrO_4^{2-} is neither oxidation nor reduction.

Question 4

The most common oxidation states of iron are +2 and +3. Using orbital box notation, draw out their respective electronic configurations and suggest which of the two ions is the more stable.

Fe^{2+}	$[Ar]3d^6$	↑↓ ↑ ↑ ↑ ↑
Fe^{3+}	$[Ar]3d^5$	↑ ↑ ↑ ↑ ↑

Answer

Fe^{3+} will be the more stable since there is a special stability associated with all the d orbitals being half filled. In Fe^{2+} only four of the d orbitals are half filled and the other is completely filled.

Page 15

Question

Suggest why scandium and zinc are not included in Table 4.

Answer

Scandium forms only the 3+ ion and zinc forms only the 2+ ion and these metals are very often considered not to be transition metals. See answer to question 2, page 14.

Page 18

Question (with answers alongside)

Name the following complexes:

(a) $[CoCl_4]^{2-}$ tetrachlorocobaltate(II)

(b) $[Ni(H_2O)_6]^{2+}$ hexaaquanickel(II)

(c) $[Fe(CN)_6]^{4-}$ hexacyanoferrate(II)

(d) $[Ti(NH_3)_6]^{3+}$ hexaamminetitanium(III)

(e) $[Ni(CN)_6]^{4-}$ hexacyanonickelate(II)

(f) MnO_4^- tetraoxomanganate(VII)

(g) $[PtCl_6]^{2-}$ hexachloroplatinate(IV)

(h) $Ni(CO)_4$ tetracarbonylnickel(0)

(i) $[Cu(NH_3)_4]^{2+}$ tetraamminecopper(II)

Questions

Q1 Methylamine, CH_3NH_2, is the simplest amine. Methylamine disturbs the ionic equilibrium in water and forms an alkaline solution in exactly the same way as ammonia. The equations for the reaction between ammonia and water are:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

a) Use equations to represent the reaction of methylamine with water. **1**

b) ***i)*** Draw a Lewis electron dot diagram for methylamine. **1**

ii) Draw a Lewis electron dot diagram for the methylammonium ion formed in the above reaction. **1**

(3)

Q2 ***a)*** Sketch the shapes of NH_3 and $BC1_3$ molecules, showing clearly all the bond angles and their values. **2**

b) Since both nitrogen and boron have three bonding electrons, why do NH_3 and BCI_3 not have the same molecular shape? **2**

SYS/90 **(4)**

Q3 Chlorine and fluorine react to produce a compound of formula CIF_3 . This molecule contains three chlorine-fluorine single bonds.

Each fluorine atom contributes one electron to the bonding.

a) How many electron pairs (both bonding and non-bonding) surround the central chlorine atom in the molecule? **1**

b) What would be the three-dimensional arrangement of electron pairs (both bonding and non-bonding) around the chlorine atom? **1**

c) The fluorine atoms may occupy different positions in this shape, giving rise to three possible shapes for the molecule. Draw two of these, showing the angles between the bonds. **2**

SYS/93 **(4)**

Q4 All three parts of the question below relate to the complex ion $[Cu(CN)_4]^{3-}$.

a) What is the oxidation state of copper in the above ion? **1**

b) How many electrons occupy the 3d energy levels of copper in this complex ion? **1**

c) How does this ion absorb energy in the visible part of the electromagnetic spectrum? **1**

SY/95 (3)

Q5 Solutions of some complex ions are acidic. For example, an aqueous solution of iron (III) chloride can have a pH of 3.0. One of the processes ocurring is:

$$[Fe(H_2O)_6]^{3+} + 3Cl^-_{(aq)} + H_2O_{(l)} \rightleftharpoons [Fe(H_2O)_5OH]^{2+} + 3Cl^-_{(aq)} + H^+_{(aq)}$$

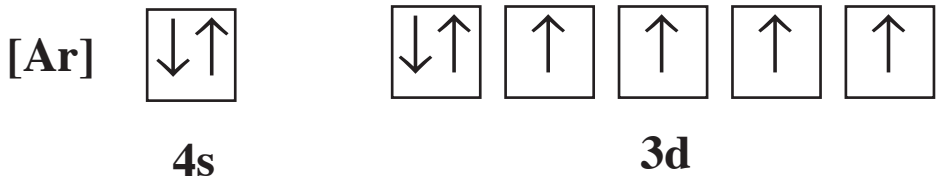
a) Name the two ligands in the complex structure on the right of the equation and explain how they act as ligands. **2**

b) Draw a diagram showing the shape of the complex ion on the right and name its shape. **2**

c) It is more difficult to remove a proton from $[Fe(H_2O)_5OH]^{2+}$ than from $[Fe(H_2O)_6]^{3+}$. Explain why this is so. **2**

SYS/87 (6)

Q6 The electronic configuration of an atom of iron may be represented by:



a) How does this arrangement for the 3d electrons follow Hund's rule of maximum multiplicity? **1**

b) Give a similar type of arrangement to represent the electronic configuration for an iron(III) ion. **1**

c) In the complex ion hexacyanoferrate(III), two of the 3d orbitals are at a higher energy level than the other three. How many unpaired 3d electrons are there in the complex ion? **1**

SY/98 (3)

Q7 Three compounds can result from the reaction between copper(II) chloride and ammonia. These compounds were reacted with silver(I) nitrate solution and the number of moles of silver(I) chloride formed per mole of each compound was calculated.

Compound	*Empirical Formula*	*Moles of AgCl*
1	$CuCl_2.4NH_3$	2
2	$CuCl_2.3NH_3$	1
3	$CuCl_2.2NH_3$	0

a) Using the above table, give the formula of the complex ion present in each compound. State a reason for your answers. **4**

b) Suggest why these three compounds have different colours from aqueous copper(II) salts. **2**

SYS/91 (6)

Q8 ***a)*** The electron configuration of a neutral chromium atom is

$$1s^2 \quad 2s^2 \quad 2p^6 \quad 3s^2 \quad 3p^6 \quad 3d^5 \quad 4s^1$$

Write down the electron configuration of chromium in the yellow chromate ion, CrO_4^{2-}. **2**

b) Explain why the colour of this ion cannot be due to d $\rightarrow$ d transitions. **1**

c) Chromate ions which are yellow change into orange dichromate ions, $Cr_2O_7^{2-}$, on the addition of acid.

Is this a redox reaction? Explain your answer. **2**

SYS/98 (5)

Q9 The ability of a ligand to split the *d* orbitals when forming a complex ion is given in the spectrochemical series. Three ligands fom this series and their relative ability to split the *d* orbital are:

$$NH_3 > H_2O > Cl^-$$

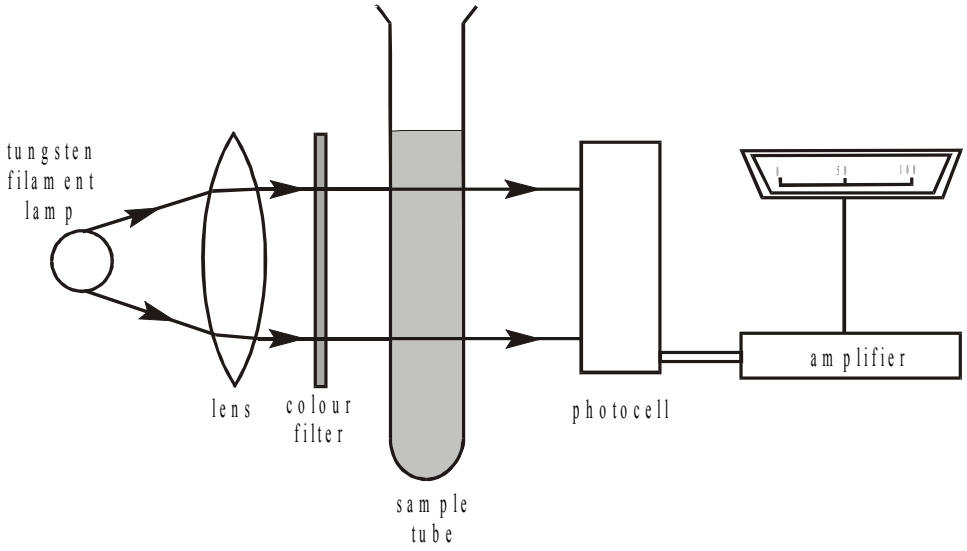
A study of part of the absorption spectrum for the complex ion, hexaaquanickel(II) shows a broad absorption band that peaks at about 410 nm.

a) Explain the origin of the absorption band at this wavelength. **2**

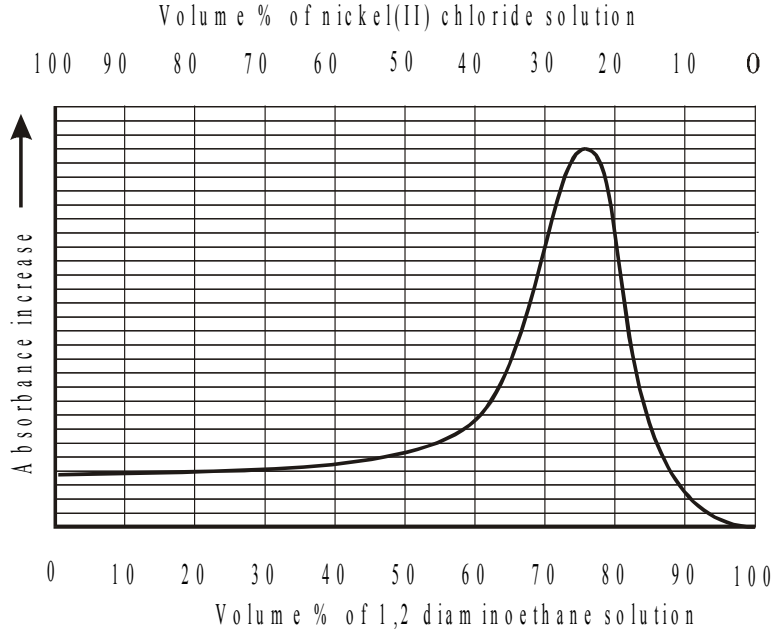
b) State towards which end of the visible spectrum the wavelength of the absorption band would move if the water ligands were replaced with chloride ions. Give an explanation for your answer. **3**

SYS/96 (5)

Q10 Solutions of nicke(II) chloride and 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$, of equal molarities were made up. From these a range of solutions of equal volume were preparedcontaining different proportions of each. Each of the resulting solutions was then placed, in turn, in a colorimeter fitted with a filter that transmitted green light.



In this way the relative absorbance of each solution was determined and the following graph drawn.



a) The formula of the complex may be represented by:

$[Ni_x(NH_2CH_2CH_2NH_2)_y]^{2+}$.

Examine the graph. What are the likely values of x and y?
Explain your reasoning briefly. **3**

b) Suggest why 1,2-diaminoethane molecules should complex with Ni^{2+} ions. **2**

c) Explain the use of the green-filter in the colorimeter. **2**

SYS/80 (7)

Q11 Account for the green colour of an aqueous solution of V^{3+} ions.
(Make reference to ligands, electrons and the visible spectrum in your answer) **3**

SYS/85 (3)

Q12 In aqueous solution, Fe^{2+} forms a deep red complex with the colourless compound phenanthroline. The intensity of the colour for a particular concentration of Fe^{2+} is independent of pH in the range 2 to 9. With the aid of a single-beam colorimeter, an analysis of a series of solutions of Fe^{2+} with phenanthroline yielded the following results:

Conc. of Fe^{2+} / g l^{-1}	*Reading on colorimeter*
0.003	31
0.005	47
0.009	84
0.015	140
solvent (water)	3
unknown	64

a) What colour of transmision filter should be used in the colorimeter? **1**

b) Evaluate the concentration of Fe^{2+} in the unknown solution. **3**

c) Suggest a reason why the solvent gave a reading. **1**

d) Suggest ***one*** improvement to the experimental method that would increase the accuracy of the result. **1**

e) Name ***one*** process responsible for the colour of transition metal complexes. **1**

SYS/90 (7)

Q13 A green solution of nickel(II) chloride was added to a colourless soluion of ammonium tetrafluoroborate, producing a pale lilac coloured complex.

a) Write down the electronic configuration for the Ni^{2+} ion. **1**

b) Give a brief explanation for the green colour of the nickel(II) chloride solution. **2**

c) Suggest a reason for the change in colour when the two solutions react together. **1**

SYS/99 (4)

Q14 The table below gives information about complex ions containing vanadium.

Ion	*Colour*
$[V(H_2O)_6]^{2+}$	violet
$[V(H_2O)_6]^{3+}$	green
$[VO]^{2+}$	blue
$[VO_2]^{2+}$	

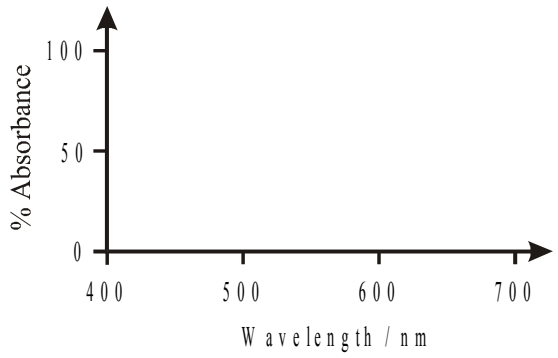
a) Determine the oxidation number of vanadium in the ions $[VO_2]^{2+}$ and $[V(H_2O)_6]^{2+}$ **2**

b) Name and draw the the shape of the green complex ion $[V(H_2O)_6]^{3+}$ **2**

c) ***i)*** Give the electronic configuration for vanadium in the $[VO_2]^{+}$ ion. **1**

ii) Suggest why you would predict this ion to be colourless. **1**

d) Light of wavelength varying from 400 to 700 nm is passed through a solution containing $[VO]^{2+}$ ions. Copy the axes shown below and draw the absorption spectrum that you would expect to obtain. (Your Data Booklet may be helpful.) **1**



SYS/97 (7)

Q15 Organic chemists now use a wide variety of catalysts when producing designer molecules. These include WC, Mo_2C, VC, W_2N and $FeCl_3$.

a) Identify an area of the Periodic Table that is common to these compounds. **1**

b) Explain in terms of electron orbitals how catalysts of this kind can affect the activation energy of a reaction. **2**

(3)

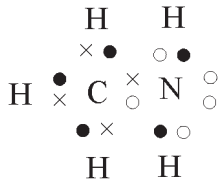
Answers

Q1 ***a)***

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$
$$+$$
$$CH_3NH_2(aq)$$
$$\downarrow\uparrow$$
$$CH_3NH_3^+(aq)$$

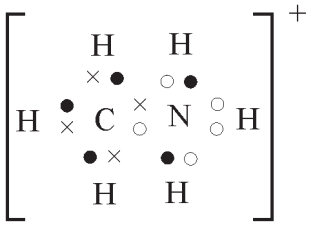
1

b) ***i)***



1

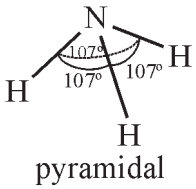
ii)



1

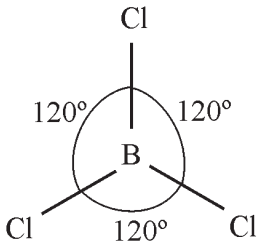
(3)

Q2 ***a)***



pyramidal

(1)



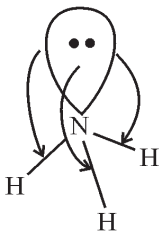
trigonal

(1)

(Do not rely on your skill as an artist – label the shapes also.)

2

b) Nitrogen has an extra pair of electrons (a lone pair). These exert a strong repulsive force downwards on the bonding pairs hence they are pushed down 'below' the tetrahedral angle, creating a pyramid:



(1)

Boron has only three outermost electrons, so BCl_3 has only three pairs of bonding electrons. They spread themselves symmetrically (or as far from each other as possible), i.e. pointing to the corners of an equilateral triangle. (1)

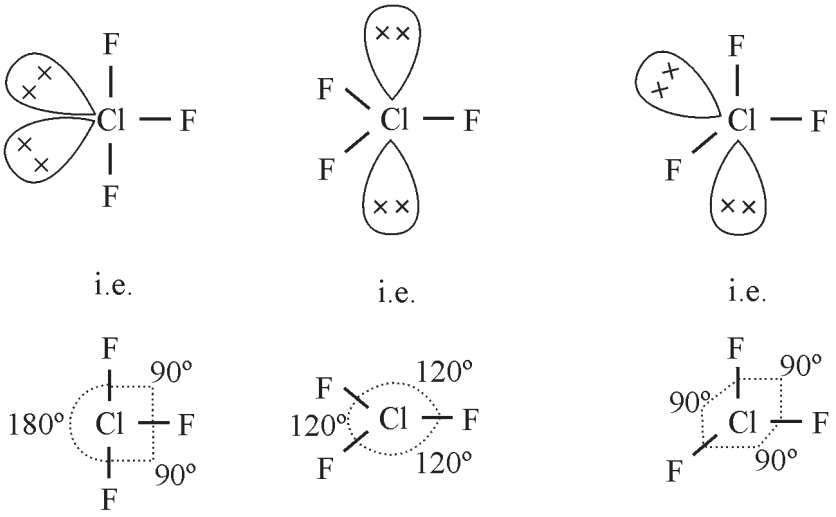
2

(4)

Q3 ***a)*** There are five pairs of electrons around the central chlorine atom (since an atom of Cl has seven outermost electrons and each F atom contributes one electron to the total ==> 7 + 3 = 10 electrons ==> 5 pairs). **1**

b) Five pairs lead to a trigonal bipyramid. **1**

c)



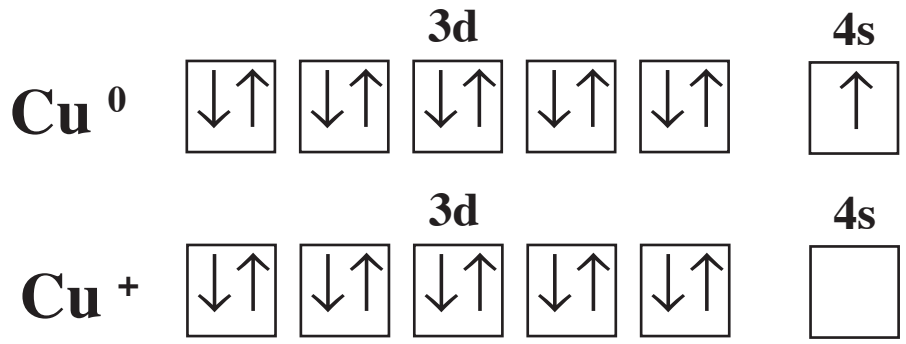
(Any two of these three shapes are acceptable.) **2**

(4)

Q4 ***a)*** +1 **1**

b) 10 **1**

c)

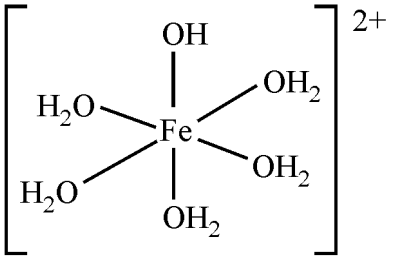


When the ion is irradiated with white light, energy is absorbed and promotes one electron from a lower 3d energy level to the higher 4s energy level. **1**

(3)

Q5 ***a)*** Water molecules and hydroxide ions. (1)
They use a lone pair of electrons to form a dative covalent bond with the central metal ion, Fe^{2+}. (1) **2**

b)



(1) octahedral (1)

2

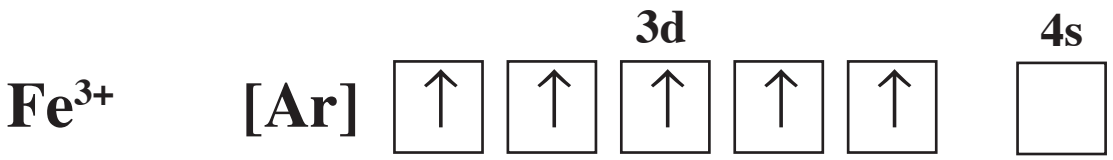
c) When a water molecule acts as a ligand its O–H bonds will become more polarised than before so H+ ions will tend to form. (1)

However, the hydroxide ion donates a complete negative charge to the central metal ion, effectively reducing the positive charge on it and so reducing the polarising effect on the O–H bonds. H^+ ions are therefore less likely to form, i.e. the solution is less acidic. (1) **2**

(6)

Q6 ***a)*** The 3d orbitals are each half-filled before one is doubly filled, i.e. maximum unpairing before pairing, etc. **1**

b)



(Note: the 4s box may precede the 3d or it may be omitted altogether since it is empty.) **1**

c) Only one **1**

(3)

Q7 ***a)*** 1. $[Cu(NH_3)_4]^{2+}$ (1)

2. $[Cu(NH_3)_3(Cl)]^{+}$ (1)

3. $[Cu(NH_3)_2(Cl)_2]^{0}$ (You may omit the zero in this formula.) (1)

Ligands are held to a central metal ion by dative covalent bonds, not by ionic bonds. The ionic chloride ions are free to form a precipitate with Ag+ ions whereas the covalently bonded chlorides are not. (1) **4**

b) The degree of d–d splitting is controlled by the ligands involved. (1)

NH_3 on its own will therefore be different from NH_3 with varying proportions of Cl. (1) **2**

(6)

Q8 ***a)*** CrO_4^{2-}

Cr = ? oxidation state

= ? + (4 × –2) = –2

? = –2 + 8

= + 6 (1)

i.e. Cr atom has lost six electrons.

$1s^2\ 2s^2 2p^6\ 3s^2\ 3p^6 3d^0\ 4s^0$ (You may omit the $3d^0\ 4s^0$.) (1) **2**

b) Cr in CrO_4^{2-} is in oxidation state +6 (see above).

In $Cr_2O_7^{2-}$, Cr = ?

(2 × ?) + (7 × –2) = –2

? = +12/2 = +6

So Cr in $Cr_2O_7^{2-}$ is also in oxidation state +6. (1)

This is therefore not a redox reaction. (1) **2**

c) d–d splitting can only apply when there is at least one electron in a d orbital (this theory similarly does not apply to a completely filled d sub-shell). **1**

(5)

Q9 ***a)*** Five degenerate orbitals are split into two orbitals of higher energy and three of lower energy. Electrons can be promoted across this gap by absorbing energy from the visible spectrum. (1)

The peak around 410 nm represents the wavelengths absorbed (and equals the energy value of the d–d split). (1) **2**

b) Since the chloro complex leads to a lower value of d–d splitting (1)

less energy is needed to make the jump (1)

so absorption moves to the lower or red end of the spectrum. (1) **3**

(5)

Q10 ***a)*** Colour intensity is at a maximum when the concentration of the complex is at a maximum. (1)

Ratio of $[Ni^{2+}]/[ligand] = 25/75 = 1/3$. (1)

i.e. $x = 1, y = 3$. (1) **3**

b) The N atoms in diaminoethane each have one lone pair. (1)

Each lone pair forms a dative covalent bond with the Ni^{2+} ion. (1) **2**

c) The complex is purple, i.e. it absorbs in the green region. (1)

The filter transmits green to get the best absorption from the complex. (1) **2**

(7)

Q11 The H_2O ligands (1)

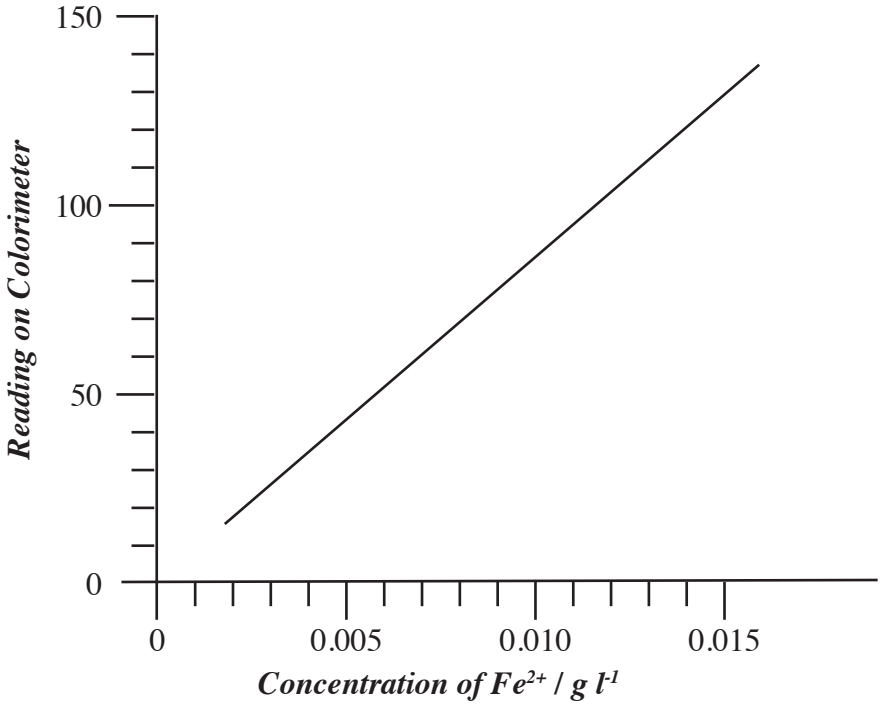
split the degenerate d orbitals. (1)

Energy from the red end of the visible spectrum is absorbed as electrons are promoted across the small energy gap, ΔE, now existing in the d orbitals. Hence the green colour is seen. (1)

3

Q12 ***a)*** Green **1**

b)



Labels/units on axes	($\frac{1}{2}$ + $\frac{1}{2}$)	
Subtracting 3 from each colorimeter reading	(1)	
Concentration of unknown = 0.0068 ± 0.0001 g l^{-1}	(1)	
(Remember to subtract 3 from the colorimeter reading for the unknown.)		**3**

c) There is some iron in the water.

or Impurities with similar absorption patterns are present. **1**

d) Duplicates should be prepared

or Large volumes should be used (to reduce error).

or A blank should be carried out on the buffer and solvent without any sample present. **1**

e) d–d splitting or d–d transitions **1**

(7)

Q13 ***a)*** Ni^{2+} [Ar] $4s^2\ 3d^8$ or $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$. **1**

b) Cl^- splits the d orbitals and energy (a selection of frequencies) from the visible spectrum promotes electrons across the gap. (1)

Remaining frequencies are transmitted and these produce the colour. (1) **2**

c) The size of the d–d split is altered by the presence of different ligands, so frequencies absorbed are different and the colour transmitted is altered. **1**

(4)

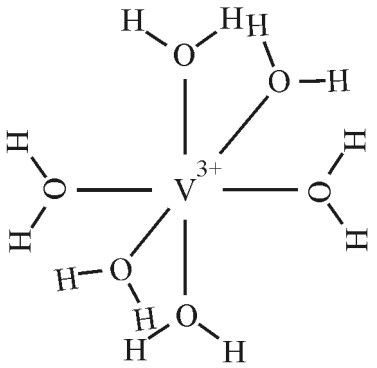
Q14 ***a)*** $[VO_2]^+$ $V + (2 \times -2) = +5$

$V = +5$ (or V) (1)

$[V(H_2O)_6]^{2+}$ V = +2 (or II) (1)

2

b) Hexaaquavanadium(III) (1)



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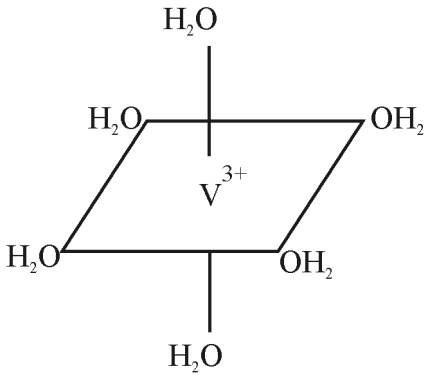


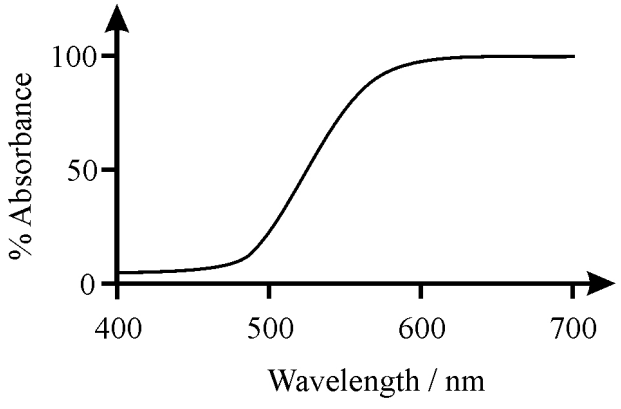
etc.

(Make sure you show that the O atom is donating the lone pair, not the H atom.) (1) **2**

c) ***i)*** $1s^2\ 2s^22p^6\ 3s^23p^6\ 4s^0\ 3d^0$ (or omit the last two terms) **1**

ii) It has no d electrons to be promoted. **1**

d) Absorption should cover the red/yellow and possibly the green regions.



1

(7)

Q15 ***a)*** They are compounds of the transition metals. **1**

b) One reactant may be adsorbed (or held by covalent bonds, often with d orbitals of the catalyst) (1)

in a suitable orientation for a more probably successful collision. ***or*** in such a way that bonds within the reactant are weakened (and there is a new arrangement of bonds, i.e. a reaction occurs). (1) **2**

(3)