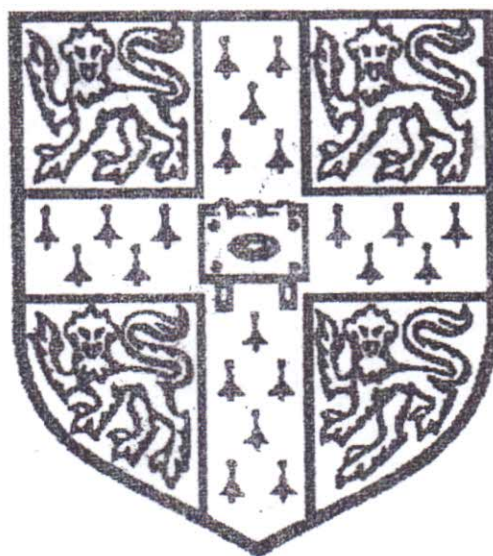


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A Level Chemistry 9254

IB
University of Cambridge
Local Examinations Syndicate



• **TRANSITION ELEMENTS**

Option Booklet

AWS

PRINCE EDWARD SCHOOL
SCIENCE DEPARTMENT
SCRUTINIZED—HEAD OF DEPT.

September 1995

Transition Elements Option Booklet**Contents****Section A: General Properties of Transition Elements**

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SECTION A: General Properties of Transition Elements

1 Introduction

The transition elements (or transition metals, as they are often called) comprise those elements in the d-block of the Periodic Table, in which the d electron shells are being filled. [The other three main blocks are: the s-block, groups I and II; the p-block, groups III to VII and group 0; and the f-block, elements 57-91 and 89-103].

More precisely, a transition element can be defined as a d-block element which forms some compounds in which there is a partly-filled sub-shell of d electrons. Thus, both scandium ($3d^0$ in Sc^{3+}) and zinc ($3d^{10}$ in Zn^{2+}) are excluded. Definitions such as this, however, can be unnecessarily restricting - zinc, for example, shows several properties that are typical of transition elements (e.g. formation of complexes with NH_3).

Turning now to the First Row of transition elements, we find that the ten elements, apart from all being obviously metallic, show more similarities in their physical properties than the other elements in their period. Just two are illustrated here:

melting point / °C

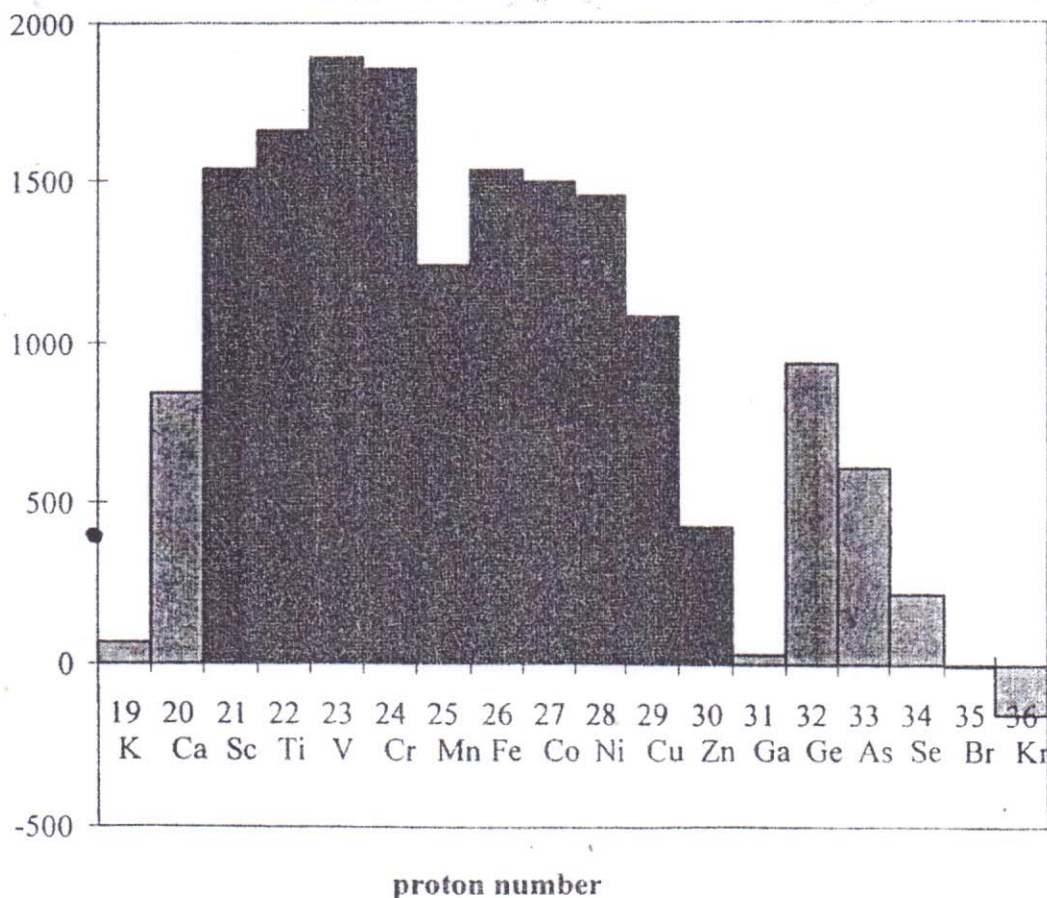


Fig. A1.1: Melting points of the elements K - Kr

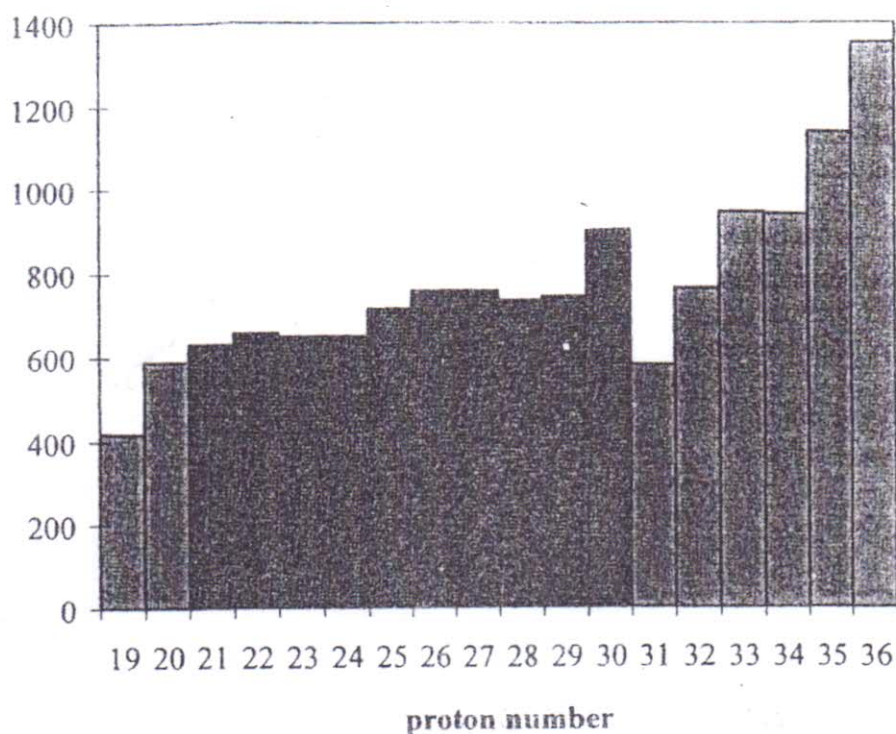
first I.E. / kJ mol^{-1} 

Fig. A1.2: First ionisation energies of the elements K - Kr

The reason for this general similarity is the relatively small difference in effective nuclear charge over this series of ten elements.

effective nuclear charge

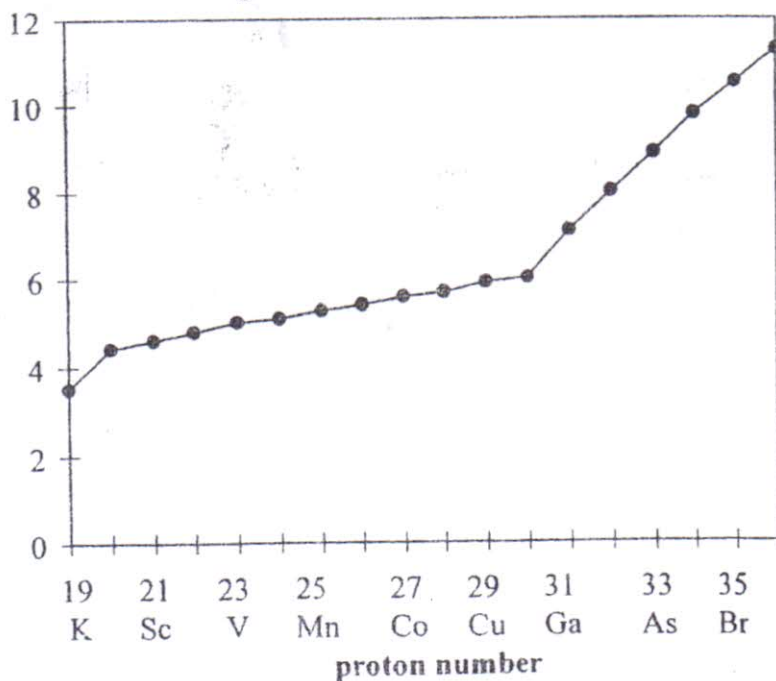


Fig. A1.3

This, in turn, occurs because each additional electron enters the penultimate 3d shell where it provides a more effective shield between the nucleus and the outer 4s shell of electrons thereby nullifying, to a considerable extent, the influence of each additional proton in the nucleus.

Although generalisations often have exceptions, it is useful to identify several physical and chemical properties in which transition elements in general differ from a typical s-block element such as calcium. These are:

- they are hard and have high densities;
- they have high melting and boiling points;
- their compounds are often paramagnetic, rather than diamagnetic (which is the more usual);
- they form compounds in which a particular element shows a variety of oxidation states;
- they form coloured compounds and ions;
- they and their compounds often show catalytic activity;
- they show a great tendency to form stable complexes.

These are considered in more detail below.

2 Physical Properties

The following table lists some properties of these elements:

element	density / g cm ⁻³	m.p. / °C	b.p. / °C	metallic radius / nm	ionisation energies / kJ mol ⁻¹		
					IE(1)	IE(2)	IE(3)
Sc	2.99	1541	2831	0.164	631	1235	2389
Ti	4.50	1660	3287	0.147	658	1310	2653
V	5.96	1890	3380	0.135	650	1414	2828
Cr	7.20	1857	2670	0.129	653	1592	2987
Mn	7.20	1244	1962	0.137	717	1509	3249
Fe	7.86	1535	2750	0.126	759	1561	2958
Co	8.90	1495	2870	0.125	758	1646	3232
Ni	8.90	1455	2730	0.125	737	1753	3394
Cu	8.92	1083	2567	0.128	746	1958	3554
Zn	7.14	420	907	0.137	906	1733	3833

Table 1

(a) Melting and boiling points

Compared to the s-block elements, the melting points and the molar enthalpies of fusion of the d-block elements are both high (see Fig. A1.1). These properties suggest strong bonding in transition elements. Metallic bonding involves delocalisation of electrons and the availability for this purpose of the 3d electrons, in addition to the 4s electrons, offers a feasible explanation of the strong bonding.

(b) Densities and metallic radii

The d-block elements are generally much denser than the s-block elements. From scandium to copper there is a gradual increase in density. The small, irregular decrease in metallic radius, coupled with increasing relative atomic mass, accounts for most of this trend.

- Q: How could you explain why the metallic radius decreases across the transition period?
- Q: What is the relationship between the density, the radius and the relative atomic mass? Use your relationship to calculate the densities of titanium, manganese and iron, and comment on the differences between the calculated and the actual densities.

(c) Ionisation energies

The noteworthy feature here is the small changes in the values of the *first* and *second* ionisation energies in the series scandium to zinc. In general, any increase in the value of a particular ionisation energy is a result of the increasing attraction of the nucleus for the electron in question. In the case of first and second ionisation energy values, it seems that the build-up of electrons in the immediately underlying d sub-shells efficiently shields the 4s electrons from the nucleus; that is, the increase in effective nuclear charge from element to element is minimal (see Fig. 1.3). The increases in the *third* ionisation energy values, from scandium to zinc, and in the *fourth* ionisation energies, from titanium to zinc, are rather more rapid (d electrons are now being removed). The remaining electrons provide relatively poor screening so that there is a significant increase in the effective nuclear charge from element to element when the third and fourth ionisation energies are being considered.

The trends in the third and fourth ionisation energies show the usual discontinuity half way along, reminiscent of the step that is observed between the first ionisation energies of nitrogen and oxygen in period 2. The reason is a similar one. The first five d electrons are all unpaired, in singly-occupied orbitals. The sixth and subsequent d electrons have to share an orbital already occupied by an electron. The resulting inter-electron repulsion means that less energy is required to remove an electron. Hence, the IE(3) curve for the last five elements is identical in shape to the curve of the first five elements, but is displaced upwards by 580 kJ mol^{-1} (see Fig. A2.1).

Thus, rather than the d^5 arrangement in the half-filled shell being particularly *stable*, as has often been said, it is more correct to describe the d^6 arrangement as being more *unstable* than might be expected.

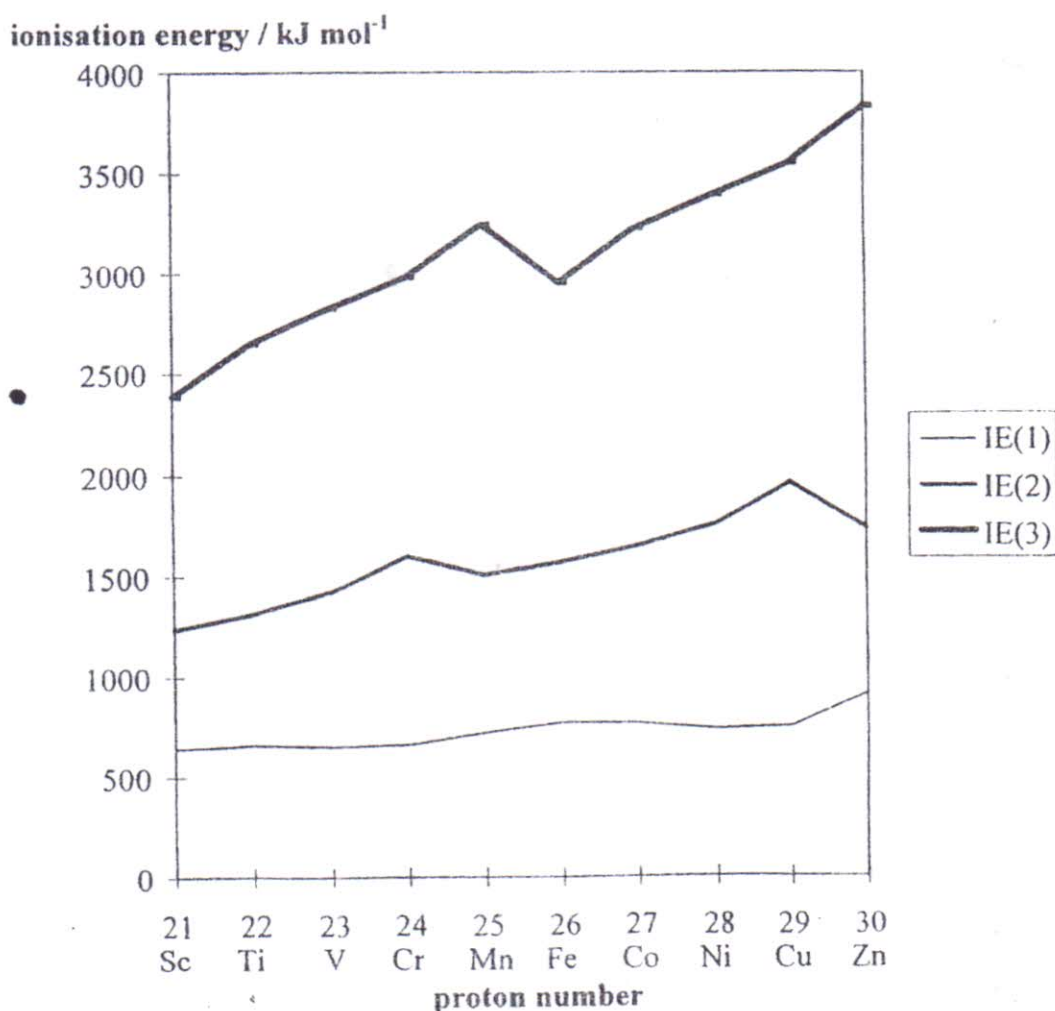


Fig. A2.1: The first three ionisation energies of the transition elements

3 *Electronic and Orbital Structures*

Much of the chemistry of the transition elements can be understood in terms of the energies of the 3d orbitals, and how they change in different ligand environments. The electronic configurations of the atoms of these elements are basically similar; they may all be represented as $(Ar)3d^x4s^y$, where (Ar) represents the electronic configuration of argon, i.e. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ and where x has one of the values one to ten, and y is two in cases except chromium and copper, where its value is one.

As the nuclear charge increases down the Periodic Table, the energies of all orbitals decrease. However, because of their proximity to the nucleus, the energies of s orbitals decrease more rapidly than other types of orbital.

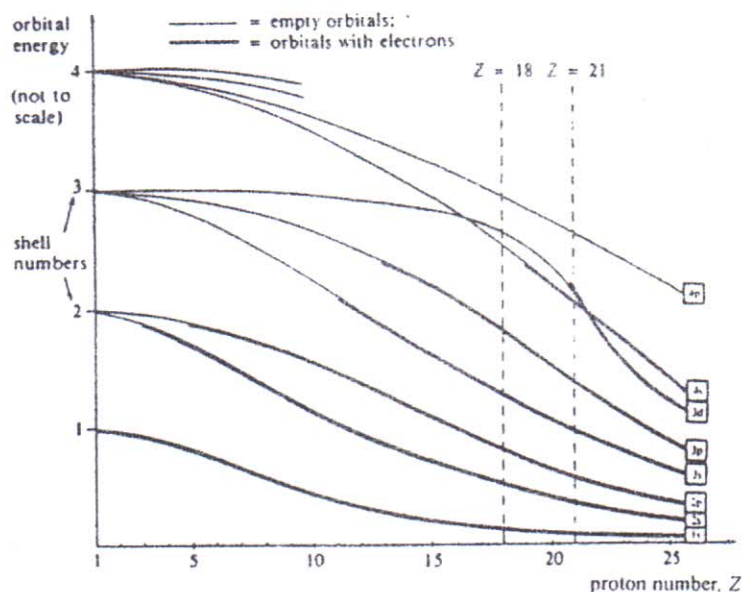


Fig. A3.1: Orbital energy decrease with Z for 1s - 4f - from Lewis and Waller, "Advancing Chemistry"

As can be seen from the above graph, the energy of the 4s orbital becomes less than that of the 3d orbital before the 3p orbital is filled, at $Z = 18$. Thus, the next electrons go into the 4s orbital. By the time chromium is reached, the 3d and 4s orbitals are about equal in energy, so occupancy of orbitals is determined more by inter-electron repulsions which favour singly-occupied orbitals, rather than energy differences between orbitals. As a consequence, the electronic configurations of the 10 elements in their ground states are:

element	1s	2s	2p	3s	3p	3d					4s
Sc	2	2	6	2	6	↑					↑↓
Ti	2	2	6	2	6	↑	↑				↑↓
V	2	2	6	2	6	↑	↑	↑			↑↓
Cr	2	2	6	2	6	↑	↑	↑	↑	↑	↑
Mn	2	2	6	2	6	↑	↑	↑	↑	↑	↑↓
Fe	2	2	6	2	6	↑↓	↑	↑	↑	↑	↑↓
Co	2	2	6	2	6	↑↓	↑↓	↑	↑	↑	↑↓
Ni	2	2	6	2	6	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	2	2	6	2	6	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	2	2	6	2	6	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Table 2

this stage, it is worth having a look at the shapes of the five d-orbitals: Four of them have a similar 4-lobed shape, whilst the fifth one ($3d_{z^2}$) consists of a dumb-bell surrounded at its waist by a small doughnut shaped ring. This is aligned along the z-axis, the lobes of one of the other orbitals align themselves along the x and y axes (the $3d_{x^2-y^2}$), leaving three orbitals (the $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$) with lobes which are pointing between the axes.

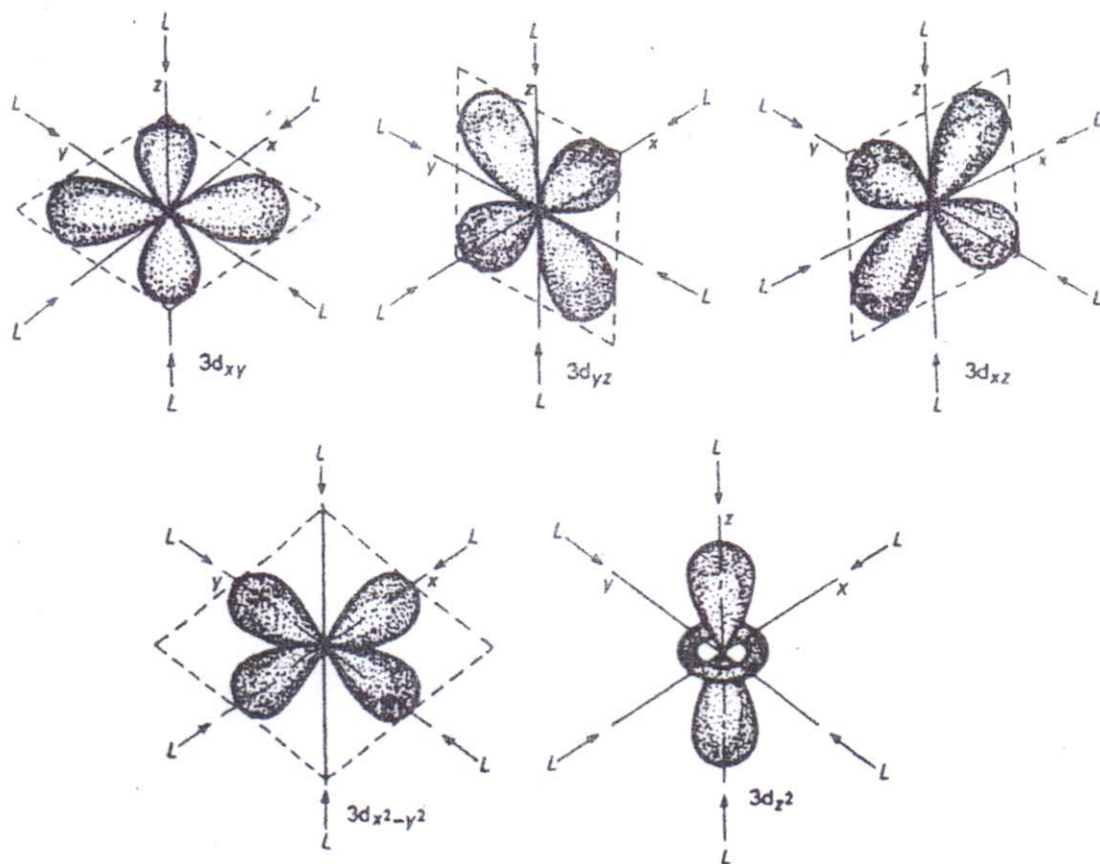


Fig. A3.2

In the isolated gas phase atoms, all five orbitals have the same energy, but in complexes they split into two (or sometimes more) groups, with an energy gap between them.

- In octahedral complexes, the lone pairs of the six ligands approach the central ion **along the axes**. Thus, the energy of an electron in either the $3d_{x^2-y^2}$, or the $3d_{z^2}$ orbital is higher than it is in the isolated atom, because of electrostatic repulsion. The energy of an electron in the other three d-orbitals is still increased, but to a lesser extent, because their lobes point **in between the axes**. Accordingly, the electron experiences less repulsion from the ligand lone pairs than it would in the $3d_{x^2-y^2}$, or the $3d_{z^2}$ orbital.
- In tetrahedral complexes, the situation is reversed. The four ligands in these complexes approach the central ion **in between the axes**. Electrons in the $3d_{xy}$, the $3d_{yz}$ and the $3d_{xz}$ orbitals now experience the greatest electrostatic repulsion from the ligand lone pairs, so have a higher energy than electrons in the $3d_{x^2-y^2}$, or the $3d_{z^2}$ orbitals.

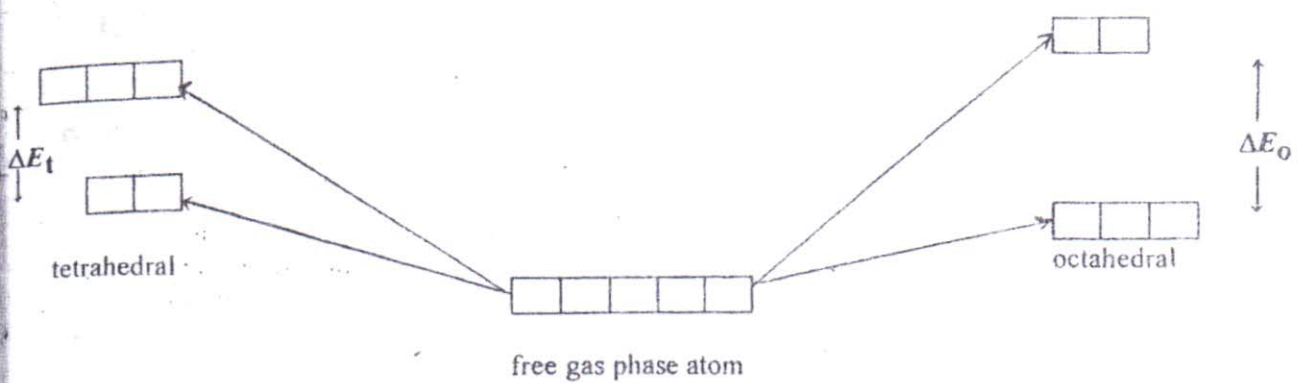


Fig. A3.3: The splitting of the five d-orbitals in tetrahedral and octahedral fields

The magnitude of the energy gap ΔE depends on the strength of the electrostatic field caused by the ligand lone pairs. For a given transition metal ion, both the colour and the magnetic behaviour depend on which ligands are complexed to it (see later).

4 Paramagnetism

When an object is placed in a strong magnetic field, for example between the poles of a horse-shoe magnet, one of three things can happen:

- it could experience no force whatsoever, in which case it is classed as being **non-magnetic**;
- it could be repelled from the magnetic field, in which case it is described as being **diamagnetic**;
- it could be attracted to the field, in which case it is described as being **paramagnetic**.

Paramagnetism is associated with unpaired electrons. Most chemical compounds are weakly diamagnetic because all their electrons are paired, but many transition element complexes are often paramagnetic. This is because they contain unpaired d electrons. It is found that the strength of the paramagnetism shown by complexes is dependent on the total number of unpaired electrons:

number of unpaired electrons	magnetic moment
1	1.73
2	2.83
3	3.87
4	4.90
5	5.92

Table 3

Q: Which of the following compounds would you expect to be paramagnetic? Arrange the paramagnetic ones in order of increasing magnetic moment: NH_3 , NO_2 , TiCl_3 , TiO_2 , VCl_3 , MnCl_2 .

As shown above, in Fig. A3.3, the five d-orbitals split into two groups in complex ions. Because of inter-electron repulsion, electrons prefer to occupy orbitals on their own. If the energy gap ΔE is large, however, it may be energetically worthwhile for the electrons to pair up in the lower orbitals. This affects the overall paramagnetism:

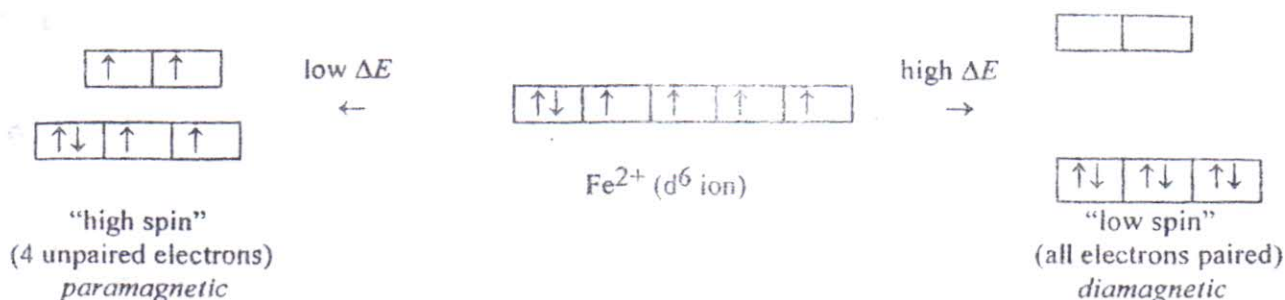


Fig. A4.1: High and low spin complexes

An extreme form of paramagnetism is **ferromagnetism**. This is shown only by the elements iron, cobalt and nickel, and by some of their oxides. This is the type of magnetic behaviour that we are most familiar with, the type that is made use of in permanent magnets, and the type that occurs in the Earth's core.

5 Oxidation States and their Relative Stabilities

The transition elements show a formidable multiplicity of oxidation states, although it is possible to discern and to explain some patterns. The reason that they are able to exhibit such a variety of oxidation states is the close similarity in energy of the 4s and the 3d electrons. The s-block elements are limited to oxidation numbers of +1 (Group I) or +2 (Group II) because, once the s electrons are removed, inner shell p electrons are then involved and their removal requires too much energy. The contrast is made clear in Table 4 below where calcium and vanadium are used as examples. It is easier to remove the **first two** electrons from calcium (total IE = 1740 kJ mol⁻¹ as against 2018 kJ mol⁻¹ for vanadium), but easier to remove the **first three** electrons in vanadium (total IE = 4888 kJ mol⁻¹ as against 6680 kJ mol⁻¹ for calcium).

element	IE ₁	IE ₂	IE ₃	IE ₄
Ca	590	1150	4940	6480
V	648	1370	2870	4600

Table 4

Table 5 summarises the known oxidation numbers of the elements scandium to zinc. Those in bold type represent the oxidation numbers considered to be of the greatest relevance for the purpose of this syllabus, although they are not necessarily either very common or very stable.

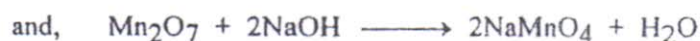
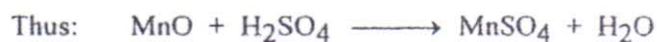
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+1	+1	+1	+1	+1	+1	+1	+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Table 5

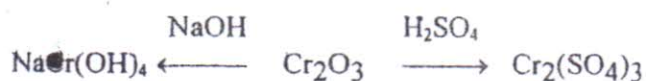
In their elemental states, the elements are conventionally assigned an oxidation number of zero. These values have been omitted from Table 2 although it should be noted that the elements chromium to copper form important compounds, the metallic carbonyls, in which their oxidation state is described as being zero.

A close scrutiny of the compounds of these elements in their many oxidation states allows a number of generalisations to be made.

- (a) The number of available oxidation states for the element increases from scandium to manganese. In manganese, both the number of oxidation states (seven) and the maximum oxidation number (+7) are exhibited in its compounds. The oxidation number +7 corresponds to the formal loss of the $3d^5 + 4s^2$ electrons. In fact, the value of the maximum oxidation number for all the elements scandium to manganese suggests that in each element all of the available 3d and 4s electrons may be used.
- (b) There is a decrease in the number of oxidation states exhibited by the elements manganese to zinc. For zinc, there is only one oxidation state and the oxidation number is invariably +2. Pairing of d electrons necessarily occurs in the element's configuration after manganese (Hund's rule*) and the decrease in the number of oxidation states exhibited by elements with more than five d electrons reflects the decreased number of unpaired d electrons available for covalent bond formation.
- (c) All of the elements except scandium show oxidation number +2, corresponding to the formal loss of the two 4s electrons.
- (d) All except zinc show oxidation number +3, although this state is unimportant in nickel.
- (e) The lower oxidation states are usually found in ionic compounds, although the ion is seldom a "simple" ion. Higher oxidation states tend to involve covalency, as might be expected from the polarising power of hypothetical cations such as Cr^{6+} and Mn^{7+} .
- (f) Oxides of elements in low oxidation states tend to be basic, e.g. MnO , but oxides of elements in high oxidation states tend to be acidic, e.g. Mn_2O_7 .



Some oxides have amphoteric character, e.g. Cr_2O_3 .



Q: Write balanced chemical equations for these two reactions of Cr_2O_3 .

- (g) The relative stabilities of different oxidation states are best understood in terms of standard electrode potentials, E^\ominus . Before describing how these are used, it is well to remember their limitations:
- The values indicate the preferred direction of reaction when all species are present in their standard states (e.g. solutions of 1 mol dm^{-3}). Large changes in pH, for example, can totally reverse the direction of a reaction. For example, E^\ominus values suggest that in 1 mol dm^{-3} solution, chlorine should oxidise $Mn^{2+}(aq)$ ions to $MnO_2(s)$, i.e. $E^\ominus(Cl_2 / Cl^-)$ is, at 1.36 V, more positive than $E^\ominus(MnO_2 / Mn^{2+})$ at 1.23 V:



*Hund's rule (of maximum multiplicity) simply means that if a set of orbitals is incompletely filled, the electrons occupy as many different orbitals in the set as possible.

whereas manganese(IV) oxide is used in the reverse of the above reaction, to prepare chlorine gas in the laboratory by the oxidation of concentrated (10 mol dm^{-3}) hydrochloric acid:



The increase in $[\text{H}^+]$ forces the reaction over to the right, in accord with Le Chatelier's principle.

- The values give no information about reaction rate. Thus, electrode potential values suggest that MnO_4^- ions should oxidise water:



In fact, solutions of potassium manganate(VII) are fairly stable for several weeks. Actual experimental conditions may be very different from the standard states to which E^\ominus values refer. A common barrier to reactivity is the oxide film which is present on metal surfaces, e.g. chromium.

Valuable conclusions about the possible course of chemical change may nonetheless be drawn from a study of E^\ominus data. When making use of such data, it is important to remember that:

- in tables of standard electrode potentials, redox half-equations are, by convention, written with the oxidised form on the left-hand side of the equilibrium sign, and
- as a consequence, a positive value of E^\ominus indicates a tendency for the redox process to occur spontaneously from left to right,

It follows that:

- oxidising agents have high positive E^\ominus values, whereas reducing agents have low or negative E^\ominus values,
- in a possible interaction between two E^\ominus redox couples, reaction can only occur between the **oxidised form of the couple with the more positive E^\ominus value** and the **reduced form of the couple with the more negative E^\ominus** . No reaction can possibly occur between the reduced form of the more positive E^\ominus couple and the oxidised form of the more negative E^\ominus couple.

The use of these ideas can be illustrated with the following selection of redox couples:

reaction or redox couple (oxidised form \rightleftharpoons reduced form)	E^\ominus/V
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+1.52
$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$	+1.23
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34
$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$	0.00
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}(\text{s})$	-1.18

The table shows manganese atoms to behave as a stronger reductant than hydrogen molecules (-1.18 is more negative than 0.00), suggesting that manganese metal should displace hydrogen from 1 mol dm⁻³ hydrochloric acid, a prediction which is realised in practice. Acidified manganate(VII) ions are stronger as an oxidant than copper(II) ions (+1.52 is more positive than +0.34), so that manganate(VII) ions should, and do, oxidise solid copper to aqueous copper(II) ions under acidic conditions. Likewise, iron(III) ions should oxidise copper metal to copper(II) ions (+0.77 is more positive than +0.34); this fact is made use of during the dissolving ("etching") of unwanted copper foil from a printed circuit board. The excess of copper is removed by using FeCl₃ solution after the circuit has been drawn on with a waxed pen. Conversely, acidified manganate(VII) ions should oxidise iron(II) to iron(III) (+1.52 is more positive than +0.77). This is the basis of a method for the quantitative estimation of iron.

Q: Write balanced chemical equations for the reactions between manganese and dilute sulphuric acid; aqueous iron(III) chloride and copper; and acidified manganate(VII) and iron(II) ions. What reactions (if any) would you expect to occur between: oxygen and iron(II) ions; oxygen and acidified manganate(VII) ions?

Further examples, including those that involve disproportionation, ligand replacement and the effect of pH, are given later.

The E^\ominus values for $M^{3+}(\text{aq})/M^{2+}(\text{aq})$ systems, as shown in Fig. 5.1, reflect the relative stabilities of the +3 and +2 oxidation states in the elements scandium to zinc, when complexed with six water ligands.

standard electrode potentials / V

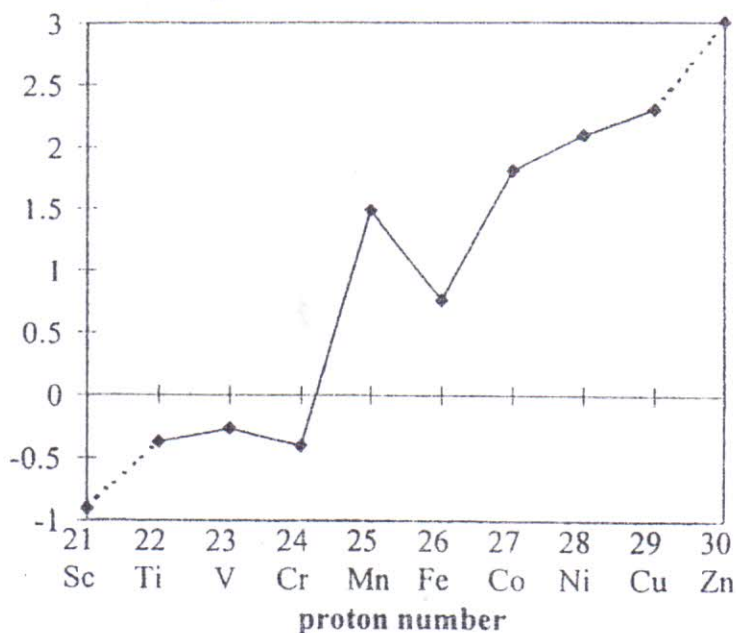


Fig A5.1: E^\ominus values for $M^{3+}(\text{aq})/M^{2+}(\text{aq})$ systems

Accurate data for the chart is necessarily incomplete, since Sc^{2+} and Cu^{3+} do not exist, and Ni^{3+} is not stable, in aqueous solution. If it existed, Sc^{2+} would be expected to be highly reducing, so the E^\ominus value for $\text{Sc}^{3+}(\text{aq})/\text{Sc}^{2+}(\text{aq})$ would be predicted to be highly negative. Likewise, Cu^{3+} would be expected to be a very strong oxidising agent, so a large positive E^\ominus value would be predicted for its $M^{3+}(\text{aq})/M^{2+}(\text{aq})$ E^\ominus . (The E^\ominus data for these two elements included in the chart have been estimated from ionisation energy and hydration energy data.)

Thus, it can be seen that the general trend is broadly similar to that of the third ionisation energies, $M^{2+}(g) \rightarrow M^{3+}(g)$ (see Fig. 2.1), including the dip from Mn to Fe, corresponding to the interelectron repulsion in the d system of Fe^{2+} , where two electrons are forced to occupy the same d-orbital (see Fig. 5.2):

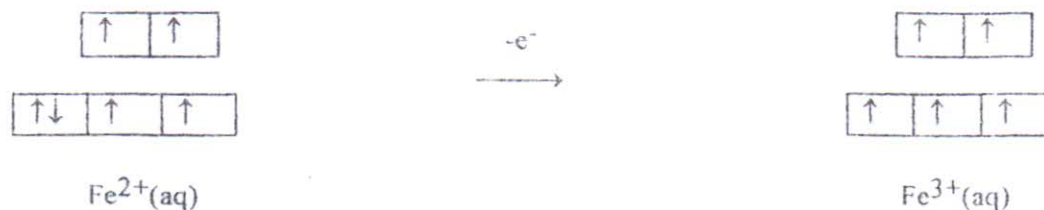


Fig. A5.2: Electron repulsion in the d^6 system

The pattern seems to be broken at chromium, in that the E^0 value for $M^{3+}(aq)/M^{2+}(aq)$ is more negative than that of vanadium. If the expected trend had continued, the value should have been above 0.0 V. However, it must be remembered that in the d^4 configuration of $Cr^{2+}(aq)$, one electron is in the higher group, so is more easily lost. Hence, $Cr^{2+}(aq)$ is a stronger reducing agent than expected.



Fig. A5.3: Easier ionisation in the d^4 system

6 Colour

Transition metal compounds are frequently coloured, both in the solid state and in solution. Their colour is entirely due to the uneven absorption of light in the visible region of the electromagnetic spectrum. If energy is absorbed in one part of the visible region, then a colour, which is the complement of the colours absorbed, is seen. A purple colour, for instance, is seen if the species absorbs in the green, yellow and orange regions but does not so at the extreme ends, i.e. in the red and blue parts of the spectrum. In most cases, the colour is caused by electrons absorbing energy as they move from one d-orbital to a higher one (remember that in a complex ionic d-orbitals are not all of the same energy, but are split into two groups - see Fig. A3.3). Such $d \rightarrow d$ transitions are responsible for the colour of many transition metal compounds. For example, blue $Cu^{2+}(aq)$ ions undergo the following electron transition when they absorb light:

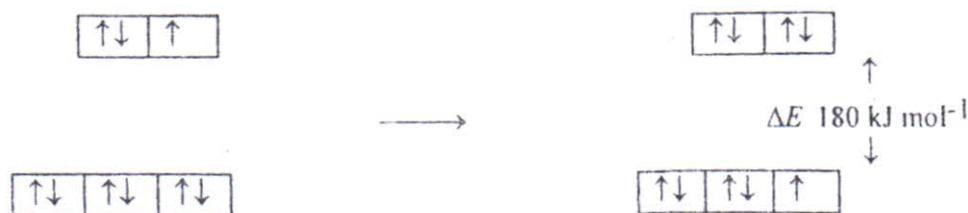


Fig. A6.1: Electron transition in the d^9 Cu^{2+} system

Using Planck's equation, we can calculate where in the spectrum this absorbance will occur, and hence the colour of the ion:

$$\text{energy gap per molecule, } \Delta E = \frac{180 \times 10^3}{6 \times 10^{23}}$$

since $\Delta E = hf$ (h = the Planck constant, f = frequency)

then $f = \Delta E/h$

$$= \frac{180 \times 10^3}{6 \times 10^{23} \times 6.6 \times 10^{-34}} \text{ Hz}$$

$$f = 4.5 \times 10^{14} \text{ Hz}$$

wavelength, λ , = c/f

$$= 3 \times 10^8 / 4.5 \times 10^{14} \text{ m}$$

$$\lambda = 6.6 \times 10^{-7} \text{ m or } 660 \text{ nm}$$

Thus $\text{Cu}^{2+}(\text{aq})$ absorbs in the red region of the spectrum (as well as the orange and yellow, because the absorption is a broad one), so the ion appears blue.

The colour of a complex can, therefore, be seen to depend on the energy gap between the two groups of d-orbitals. This in turn depends on the following factors.

(a) *The nature of the metal and its oxidation state*

Taking the +2 and +3 oxidation states of chromium and iron as examples: $\text{Cr}^{2+}(\text{aq})$ is sky-blue ($\Delta E = 190 \text{ kJ mol}^{-1}$), whereas $\text{Cr}^{3+}(\text{aq})$ is green ($\Delta E = 205 \text{ kJ mol}^{-1}$). $\text{Fe}^{2+}(\text{aq})$ is pale green, whereas $\text{Fe}^{3+}(\text{aq})$ is violet.

(b) *The nature of the ligand*

Different ligands have different effects on the relative energies of d orbitals of a particular ion. For example, ammonia ligands cause a larger difference than water molecules in the relative energies of the two groups of d orbitals in the ligand field. This factor results in the colour change from blue to blue-violet when ammonia is added to an aqueous solution of a copper(II) salt.

In order to absorb light in the first place, the metal ion has to contain not only at least one d electron, but also a space in the higher d orbital. The absence of colour in $\text{Sc}(\text{III})$, $\text{Cu}(\text{I})$ and $\text{Zn}(\text{II})$ compounds is due to the fact that they have either no d electrons ($\text{Sc}(\text{III})$), or a d^{10} arrangement ($\text{Cu}(\text{I})$, $\text{Zn}(\text{II})$). In either case, no $d \rightarrow d$ transition is possible. The almost complete lack of colour in $\text{Mn}(\text{II})$ compounds is due to a more subtle reason. Each of the five d-orbitals in $\text{Mn}(\text{II})$ compounds contains just one electron. In a particular ion, these five electrons tend to align their spins parallel to each other. If an electron were to move from one of the lower set of orbitals to the higher set, it would have to change the direction of its spin, because an orbital cannot be occupied by two electrons unless their spins are opposite. The changing of an electron's spin in isolation of other spin changes is almost totally forbidden by the rules of quantum mechanics. Thus, $\text{Mn}(\text{II})$ compounds have only a very pale pink colour.



Fig. A6.2: Electron transition in the $d^5 \text{Mn}^{2+}$ system

There are many examples of colours in transition metal compounds where $d \rightarrow d$ transitions are not involved, e.g. MnO_4^- in which a charge transfer mechanism operates. In this situation, an electron in a bonding orbital (between the ligand and the metal ion) is promoted to one of the higher d orbitals (located on the metal ion itself). In this way, negative charge is "transferred" to the metal. Other possible colour-causing effects include the presence of mixed oxidation states (as in Prussian Blue, a mixed cyanide complex of Fe(II) and Fe(III)), and lattice defects.

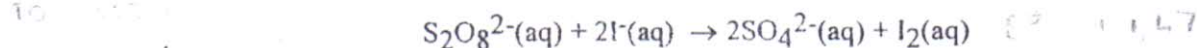
7 Catalysis

Transition elements, both in the elemental form and in their compounds, are effective and important catalysts. A catalyst is a substance which ~~increases~~ ^{ALTERS} the rate of a reaction without itself undergoing any permanent chemical change. They achieve this by offering an alternative pathway for the reaction, one which involves a lower activation energy than that of the uncatalysed process. There are two types of catalysts: **heterogeneous catalysts** operate in a different physical phase to the reactants (most commonly the catalysts are solids, and the reactants are gases), whereas **homogeneous catalysts** operate in the same phase as the reactants. Two features of transition elements seem to be especially important in their role as catalysts.

For **heterogeneous catalysis** to occur, the reactant molecules need to be readily adsorbed onto the catalyst surface. This is achieved through the availability of partially-filled $3d$ orbitals, which allows the ready exchange of electrons to and from ligand molecules, forming weak bonds with the ligands. This adsorption in turn weakens the bonds in the reactant molecules, thereby lowering the activation energy, as well as increasing the surface concentration of reactants. As a consequence, the reactant molecules are brought closer together. Important examples of this type of catalysis are plentiful in the chemical industry; vanadium(V) oxide in the Contact process; iron/iron oxide in the Haber process and nickel in the hydrogenation of alkenes.

The ability of transition metals to vary their oxidation state is the key factor in their efficiency as **homogeneous catalysts**. The oxidation of I^- by $\text{S}_2\text{O}_8^{2-}$ can be used as an example of catalytic behaviour in homogeneous systems.

The redox reaction:



is accelerated by the presence of a number of transition metal compounds. Iron(II) (and iron(III)) compounds, for example, are found to be effective. A study of the relevant reduction potentials suggests a possible explanation.

	system	E^0/V
1	$\frac{1}{2}\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \leftrightarrow \text{SO}_4^{2-}$	+2.01
2	$\text{Fe}^{3+} + \text{e}^- \leftrightarrow \text{Fe}^{2+}$	+0.77
3	$\frac{1}{2}\text{I}_2 + \text{e}^- \leftrightarrow \text{I}^-$	+0.54

Comparison of steps 1 and 3 confirms that the uncatalysed reaction is able to go to completion but, as always, such considerations tell us nothing about rate. A possible catalysed pathway, having lower activation energy, involves two steps. If $\text{Fe}^{2+}(\text{aq})$ is present as catalyst, the first step is:



and the second is:



Reference to the E^{\ominus} values (above) shows that these processes are energetically feasible and, furthermore, the proposed scheme shows the regeneration of the catalyst $\text{Fe}^{2+}(\text{aq})$. $\text{Fe}^{3+}(\text{aq})$ clearly should also be effective, the two steps suggested above now occurring in reverse order. As to why this alternative 2-step route offers a lower energy pathway, one likely explanation is that it avoids the direct reaction between two ions of the **same** electrostatic charge: I^{-} and $\text{S}_2\text{O}_8^{2-}$ are likely to repel each other in solution, but the two steps occurring during the catalysed route involve reactions between **oppositely** charged ions, the natural tendency of which is to attract each other. It would be anticipated that other couples involving transition metal cations would also act as catalysts, as long as their E^{\ominus} values were intermediate between 0.54 V and 2.01 V.

Q: Using E^{\ominus} values from the Data Booklet, or those listed under specific elements in Part B of this booklet, suggest two other redox couples that could catalyse this reaction.

8 Complexes

Another characteristic feature of d-block elements is the widespread occurrence of complex compounds. A complex species may be neutral, e.g. $\text{Ni}(\text{CO})_4$; cationic, e.g. $[\text{Ag}(\text{NH}_3)_2]^+$; or anionic, e.g. $[\text{CuCl}_4]^{2-}$. A complex is formed by the combination of a central atom or ion with surrounding ions or molecules, these surrounding particles being termed **ligands**. Two important features of a complex are as follows.

- (i) *The net charge on the complex:* this is the resultant of the charge contributions from the ligands and from the central particle. The "charge" on the central particle is, of course, the oxidation number of the metal in that complex ion.
- (ii) *The co-ordination number:* this indicates the number of ligand groups around the central atom or ion. The most common values are four and six, but two is also widespread and is particularly important in the chemistry of copper(I) and silver(I) compounds.

All cations have some tendency to form complexes, since they attract the electron charge clouds on surrounding groups. However, this tendency is particularly strong amongst d-block elements. The "bare" cations of transition elements, with their outermost incomplete d sub-shells, are relatively small and highly charged. The resulting high charge density, and hence polarising power, produces a strong tendency towards covalent bond formation. Cations of s-block elements, in contrast, are larger, have a lower polarising power and thus tend to become involved in ion-dipole bonding, rather than covalency. Transition metal ions accept electron pairs from the ligands in the form of dative covalent bonds. A **ligand** can be a neutral molecule or an anion. It must possess at least one unshared (non-bonding) pair of electrons. Ligands are classified according to the number of bonds that they are able to form with the central atom or ion:

number of bonds formed by ligand	ligand type	examples
1	monodentate	$\text{NH}_3, \text{H}_2\text{O}, \text{Cl}^-, \text{CN}^-$
2	bidentate	$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2, ^-\text{O}-\text{CO}-\text{CO}-\text{O}^-$
3	tridentate	$\text{NH}_2(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$
6	hexadentate	EDTA
many	polydentate	

Table 6

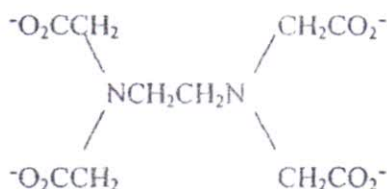


Fig A8.1: Structural formula of EDTA

The number of bonds formed must not be equated, of course, with the number of non-bonding pairs of electrons the ligand - each co-ordinating atom can only donate one lone pair to the central ion, even if it has more, and there may be some atoms with lone pairs in the ligand that donate none.

(a) Stoichiometry of Complexes

Stoichiometry is the study of the ratios in which molecules and ions react together. Discovering the stoichiometry of a complex ion is the first step in finding out its structure. Thus, experimental work showing the stoichiometry in the complexes of copper(II) with ammonia and with chloride was a great help in understanding the aqueous chemistry of copper. As illustrated below, however, there can often be several structures having same stoichiometry, showing various types of isomerism.

(b) Stereochemistry of Complexes

The electron pair repulsion model is used in order to understand and to predict the shapes of molecules involving s- and p-block elements. With d-block elements, which contain non-bonding d electrons, this approach is possible since d electrons differ from s and p electrons in their influence on molecular shape. However, at elementary level, the range of stereochemistry encountered is limited and the generalisations shown in Table 7 provide an adequate summary.

co-ordination number	shape
2	Linear
4	Tetrahedral (more usual) or square planar
6	Octahedral

Table 7

Many of the shapes are entirely regular, but some important species have a lower degree of symmetry and alter according to the environment. For example, in the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, there are four 'short' and two 'long' copper to oxygen bonds, thereby producing a distorted octahedral arrangement. The dislike of Cu^{2+} to

surrounded by six equal-strength bonds also helps to explain why only 4 of the 6 water ligands (the 4 "short" bonded ones) are replaced by ammonia molecules in the tetra-amminecopper(II) ion. In order to replace all six water ligands, pure liquid ammonia must be used. This is an example of the Jahn-Teller effect, and can be pursued further in more advanced texts.

(c) Isomerism in Complexes

The existence of two geometries for coordination number 4, and a very large number of hexaco-ordinate complexes, results in the appearance of a variety of isomeric behaviour. Examples of the various types of isomerism that have been observed in transition metal complexes are as follows.

(i) conformational isomerism

This uncommon isomerism occurs when a complex can be prepared in two different geometries. Thus the complex $\text{NiCl}_2(\text{R}_3\text{P})_2$ can exist not only in a green, paramagnetic tetrahedral form, but also in a brown, diamagnetic square planar form:

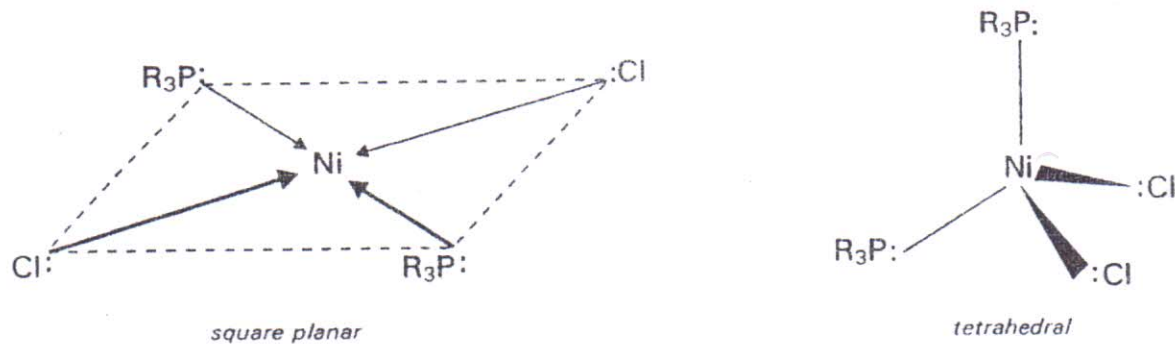


Fig A8.2: Square planar and tetrahedral forms of $\text{NiCl}_2(\text{R}_3\text{P})_2$

(ii) geometrical (cis-trans) isomerism

This occurs mainly in square-planar and octahedral complexes, where ligands can occupy positions adjacent (*cis*) to each other or on opposite sides of the central ion (*trans*). These isomers usually differ in dipole moment as well as colour. As an example, the dichlorotetra-amminecobalt (III) ion exists in both *cis* and *trans* forms.

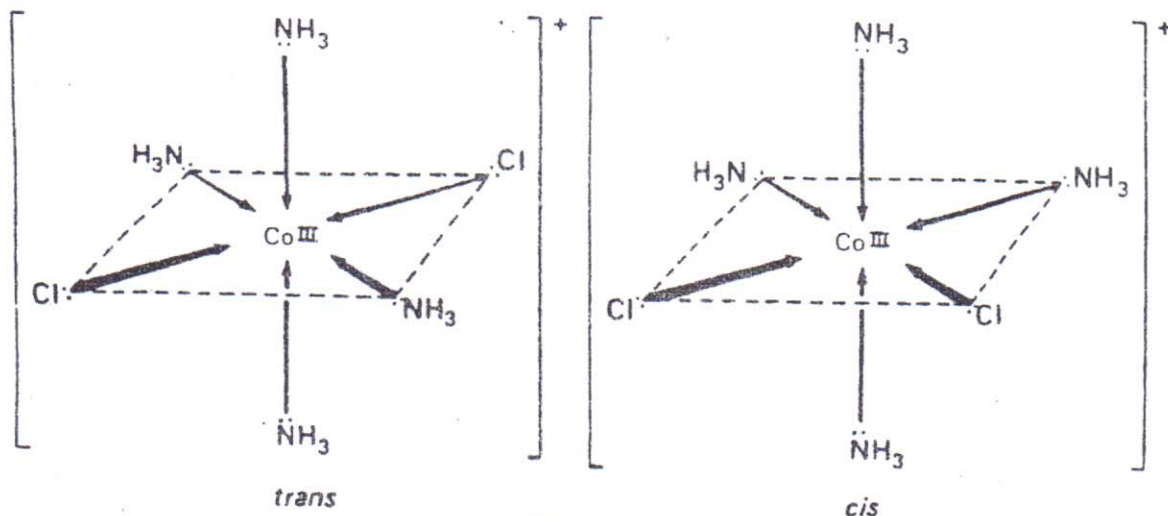


Fig A8.3

Does the dichlorodiammine platinum(II) complex, the *cis* isomer of which is used as an effective agent in the chemotherapy of cancer patients:

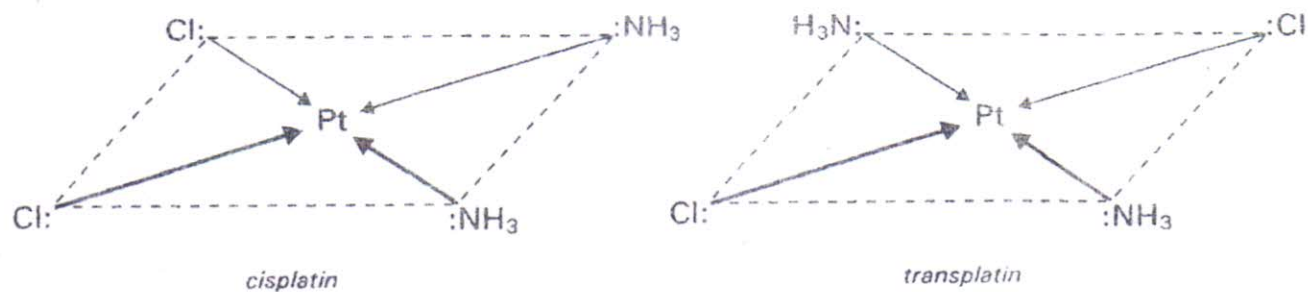
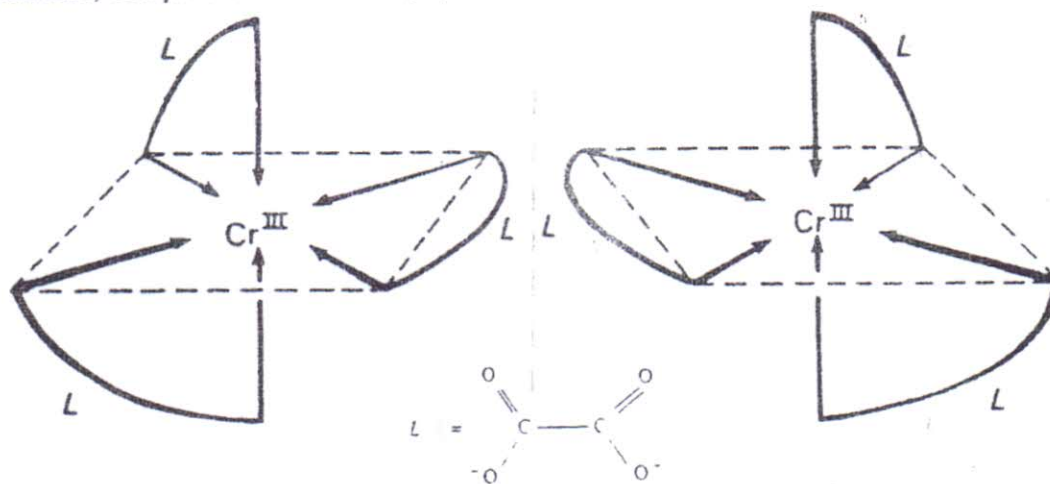


Fig A8.4

(iii) optical isomerism

Octahedral complexes containing at least two bidentate ligands (which cannot occupy two *trans* positions due to the closeness of their ligand atoms to each other) have neither a centre nor a plane of symmetry. They are thus chiral molecules, capable of existing in two non-superimposable mirror-image forms. This can be illustrated by the tris(ethanedioato) complexes of chromium(III):

Fig A8.5: + and - forms of $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

The cation of the compound $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+\text{Cl}^-$ can exist in three forms, two of which are optically active mirror images with dipole moments, and the third is optically inactive with no dipole moment.

Q: Draw diagrams to show the different arrangements of the ligands in these three forms, and explain their observed physical properties as described above.

(iv) ionisation isomerism

This occurs when isomers produce different ions in solution, and is due to one or more ligands being able to exchange positions with counter ions (or even hydrating water molecules) outside the co-ordination sphere. Thus, $[\text{PtCl}_2(\text{NH}_3)_4]^{2+}(\text{Br}^-)_2$ and $[\text{PtBr}_2(\text{NH}_3)_4]^{2+}(\text{Cl}^-)_2$ are isomers (each of which, incidentally, can exist in *cis* or *trans* forms!), as are the members of the series: $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{Cl}^-)_3$ {violet}, $[\text{CrCl}(\text{H}_2\text{O})_5]^{2+}(\text{Cl}^-)_2$ {pale green} and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+\text{Cl}^-$ {dark green}.

Q: The covalent Cr-Cl bond is slow to react. How could the above three complexes be distinguished through the use of silver nitrate solution?

(v) *coordination isomerism*

This occurs when both cation and anion are complexes, and each central ion can be complexed by each other's ligands. Examples include $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{CN})_6]^{3-}$; $[\text{Cu}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{CuCl}_4]^{2-}$.

(vi) *polymerisation isomerism*

This is closely related to co-ordination isomerism. It occurs when a cation-anion pair has the same empirical formula as a single-metal-atom complex, but with twice the relative formula mass. For example, the complex $[\text{Pt}(\text{NH}_3)_4]^{2+}[\text{PtCl}_4]^{2-}$ has the same empirical formula as either the *cis* or the *trans* form of $[\text{PtCl}_2(\text{NH}_3)_2]$. There are seven known compounds with the stoichiometry $\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3$, of which several have the molecular formula $\text{Co}_2(\text{NH}_3)_6(\text{NO}_2)_6$, with various numbers of ammonia and nitrite ligands in the cation and the anion.

Q: Draw structures for four such complexes, and predict whether each ion you have drawn has a dipole moment.

(d) *Stability constants*

Complex ions differ considerably in their stability. In complex ion equilibria, as in acid-base and redox equilibria, the extent of change may be described by an equilibrium constant. Consider the ion $\text{Ag}(\text{H}_2\text{O})_2^+$, present in aqueous solutions of silver(I) salts. Addition of ammonia to such a solution brings about a stepwise replacement of water ligands by ammonia ligands, as shown below.



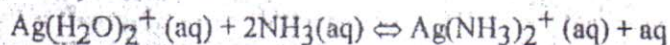
The equilibrium constants for steps 1 and 2, K_1 and K_2 respectively, are

$$K_1 = \frac{[\text{Ag}(\text{H}_2\text{O})(\text{NH}_3)^+]_{eq}}{[\text{Ag}(\text{H}_2\text{O})_2^+]_{eq} [\text{NH}_3]_{eq}}$$

$$\text{and } K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]_{eq}}{[\text{Ag}(\text{H}_2\text{O})(\text{NH}_3)^+]_{eq} [\text{NH}_3]_{eq}}$$

where the suffix *eq* denotes an equilibrium value.

Q: Show that for the overall replacement:



the equilibrium (stability) constant K is equal to $K_1 \times K_2$.

The course of ligand replacement reactions may be considered in terms of competition for sites on the central ion by the ligands present. The value of a stability constant, similar to those defined above, is clearly an indication of the inherent tendency of a particular ligand to replace water in the aquo-complex. The stability of chelate complexes, involving polydentate ligands, is usually greater than that of complexes based on monodentate ligands. This can be seen in the following table.

Stability constants vary in magnitude over several powers of 10, and it is often more convenient to use the logarithm of the stability constant ($\lg K$) to allow an easier comparison. Table 8 gives some values for a number of common complex ions. The larger the value of $\lg K$, the more stable the complex is relative to the 'simple' aqueous ion.

Monodentate ligands

element	ion	K	$\lg K$
Cr	$[\text{Cr}(\text{OH})_4]^-$	1×10^{-2}	-2
Fe	$[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$	8×10^3	3.9
	$[\text{Fe}(\text{H}_2\text{O})\text{F}_3]^{2-}$	2.2×10^{15}	15.3
	$[\text{FeCl}_4]^-$	8×10^{-2}	-1.1
	$[\text{Fe}(\text{CN})_6]^{4-}$	1×10^{24}	24
	$[\text{Fe}(\text{CN})_6]^{3-}$	1×10^{31}	31
Co	$[\text{Co}(\text{NH}_3)_6]^{2+}$	8×10^4	4.9
	$[\text{Co}(\text{NH}_3)_6]^{3+}$	5×10^{33}	33.7
	$[\text{Co}(\text{CN})_6]^{3-}$	1×10^{64}	64
Ni	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	5×10^7	7.7
	$[\text{Ni}(\text{CN})_4]^{2-}$	1×10^{31}	31
Cu	$[\text{Cu}(\text{NH}_3)_2]^+$	1×10^{11}	11
	$[\text{Cu}(\text{CN})_4]^{3-}$	1×10^{27}	27
	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	1.2×10^{13}	13.1
	$[\text{CuCl}_4]^{2-}$	4.2×10^5	5.6
Zn	$[\text{Zn}(\text{NH}_3)_4]^{2+}$	4×10^9	9.6

Bidentate ligands

element	ion	K	$\lg K$
Ni	$[\text{Ni}(\text{en})_3]^{2+}$	6×10^{18}	18.8
Cu	$[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$	4×10^{19}	19.6

Hexadentate ligands

element	ion	K	$\lg K$
Cr	$[\text{Cr}(\text{edta})]^{2-}$	1×10^{13}	13
	$[\text{Cr}(\text{edta})]^-$	1×10^{24}	24
Mn	$[\text{Mn}(\text{edta})]^{2-}$	1×10^{14}	14
Fe	$[\text{Fe}(\text{edta})]^{2-}$	2×10^{14}	14.3
	$[\text{Fe}(\text{edta})]^-$	1.3×10^{25}	25.1
Co	$[\text{Co}(\text{edta})]^{2-}$	2×10^{16}	16.3
	$[\text{Co}(\text{edta})]^-$	1×10^{36}	36
Ni	$[\text{Ni}(\text{edta})]^{2-}$	4×10^{18}	18.6
Cu	$[\text{Cu}(\text{edta})]^{2-}$	6×10^{18}	18.8

Table 8

SECTION B: Details of Some Individual Transition Elements

This section considers selected aspects of the chemistry of eight members of the first transition series. The following general points should be noted.

- Compounds of the metals in low oxidation states (+2 and +3) may be regarded as largely ionic and it is important to be familiar with the reactions of the common aquated cations.
- All these cations have precipitation reactions, e.g. with aqueous ammonia, followed frequently by ligand replacement reactions in which soluble complexes are formed.
- Acid-base character is especially prominent in the chemistry of $\text{Cr}^{3+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$.
- Redox reactions are extremely important in cases where there is a higher or lower oxidation state of appreciable stability. Such relationships should be considered in relation to E^\ominus values.
- The high oxidation states are, of course, oxidising and the emphasis in this section is on the behaviour of oxoanions such as MnO_4^- and CrO_4^{2-} in redox reactions.

1 Titanium

(a) origin/occurrence

Titanium is the ninth most abundant element in the Earth's crust, with an abundance of 0.63%. Its main ores are ilmenite, FeTiO_3 , and rutile, TiO_2 .

(b) extraction

The Kroll method, developed in 1932, involves the following two-stage extraction. Titanium(IV) oxide is mixed with coke and the mixture reacted with chlorine at 800 °C to 1000 °C. The major reaction is:



The titanium(IV) chloride formed is purified and stored in steel tanks under argon. The major chemical step is the reduction of the chloride. A powerful reductant is needed and both magnesium and sodium are used in different processes. In the magnesium process, pure magnesium ingots are sealed into a strong steel pot. Argon is introduced to provide an inert atmosphere and the pot heated to 700 °C.

Liquid titanium(IV) chloride is added, whereupon a strongly exothermic reaction occurs, which needs careful control in order to maintain the temperature in the range 850 °C to 900 °C.



The magnesium chloride is tapped off from time to time and is, of course, re-cycled. Molten magnesium chloride is electrolysed, yielding chlorine, for production of the titanium(IV) chloride and magnesium for the main reduction. The impure metal obtained may be purified by vacuum distillation, giving so-called 'raw' titanium. This is converted into a usable metal by remelting, in a vacuum or a noble gas atmosphere, in an electric arc furnace.

(c) uses

Titanium has a density about half that of steel and, since it shows about the same mechanical strength, has a superior strength-to-weight ratio. It has a high melting point, 1675 °C, and is chemically unreactive at moderate temperatures. However, it does become considerably more reactive at higher temperatures and its ready formation of interstitial compounds with oxygen, nitrogen, carbon, etc. is a major disadvantage. The formation of such compounds renders the material excessively brittle and also decreases its resistance to corrosion. However, its properties may be improved generally by alloying, especially with aluminium and tin. Titanium remains relatively expensive to produce and there is no immediate prospect that it will replace iron as a structural material.

Predictably, its main uses are in the manufacture of aircraft, space capsules, aeroengines (turbine blades) and in industrial plant. The graphite anode formerly used in the familiar Diaphragm Cell for the production of sodium hydroxide and chlorine has been superseded by a more efficient platinum-coated titanium anode.

Worldwide annual production of the metal is of the order of 10^5 tonnes. There is an enormous demand for purified titanium(IV) oxide as a white pigment, especially in paints and as a surface coating on paper. Production is over 3×10^6 tonnes of TiO_2 per year.

(d) redox chemistry

Titanium forms three series of compounds in which the metal shows oxidation states of +2, +3 and +4 respectively. Consideration of the E^\ominus values quoted below allows understanding of the relationship between these three oxidation states.

	reaction of titanium systems	E^\ominus/V	reaction of other systems
1		+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
2	$\text{TiO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ti}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.10	
3		0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
4	$\text{Ti}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ti}^{2+}(\text{aq})$	-0.37	
5	$\text{Ti}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ti}(\text{s})$	-1.63	

The highly negative redox potential for titanium metal may seem at odds with its industrial use. Like aluminium and chromium, however, the readily-formed oxide produces a thin impervious layer that stops any further corrosion and makes titanium one of the most inert metals in common use. Consideration of redox potentials 3 and 5 (above) indicates that titanium metal should cause the evolution of hydrogen under standard acid conditions; titanium does indeed displace hydrogen from dilute sulphuric acid.

Comparison of potentials 3 and 4 suggest that any $\text{Ti}^{2+}(\text{aq})$ ions formed would reduce $\text{H}^+(\text{aq})$, being themselves oxidised to $\text{Ti}^{3+}(\text{aq})$ ions. In fact, the reducing power of $\text{Ti}^{2+}(\text{aq})$ is such that there is no aqueous Ti(II) chemistry although *anhydrous* Ti(II) compounds are known. It might be expected that $\text{Ti}^{3+}(\text{aq})$ would be stable. However, under ambient conditions, further oxidation to Ti(IV) is observed, an event which might be predicted from comparison of the quoted E^\ominus values for reactions 1 and 2. Ti(IV) is the stable oxidation state in the presence of oxygen.

Q: Use the above half-equations to construct a balanced equation for the oxidation of Ti^{3+} by oxygen.

(e) complexes

In solution in water, Ti(III) salts contain the octahedral, purple complex ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. This also occurs in hydrated salts. $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ shows ionisation (hydrate) isomerism (see Section A8 (c)(iv)), existing as the violet $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$ and the green $[\text{TiCl}_2(\text{H}_2\text{O})_4]^+ \text{Cl}^-$. Anionic complex ion such as $[\text{TiF}_6]^{3-}$ are also known. All complexes of Ti(III) are paramagnetic, with a magnetic moment consistent with the presence of one unpaired electron.

Ti(IV) also forms octahedral complexes, as in $[\text{TiF}_6]^{2-}$. As might be expected for a d^0 system, these are diamagnetic. The ion Ti^{4+} is intensely polarising with the consequence that $[\text{Ti}(\text{H}_2\text{O})_6]^{4+}$ cannot exist. This is similar to the case of V^{4+} and V^{5+} and, as in vanadium chemistry, the usual representation of Ti(IV) by one particular formula, TiO^{2+} , is an over-simplification. Aqueous solutions of Ti(IV) in chloric(VII) acid, HClO_4 , have been shown to contain either $\text{TiO}^{2+}(\text{aq})$ or $\text{Ti}(\text{OH})_2^{2+}(\text{aq})$.

(f) other compounds and reactions

Titanium(IV) chloride (m.p. $-24\text{ }^{\circ}\text{C}$, b.p. $137\text{ }^{\circ}\text{C}$) is similar to SiCl_4 and other Group IV chlorides - a colourless volatile covalent liquid rapidly hydrolysed by water:



Apart from its use during the extraction of titanium, TiCl_4 is used to produce Ziegler-Natta catalysts for the polymerisation of ethene.

(g) summary of the chemistry of titanium

- main oxidation states are +2, +3 and +4, the first two being easily oxidised by air to the +4 state
- main stereochemistry of complexes is octahedral
- Ti(III) is paramagnetic and purple in aqueous solution, Ti(IV) is diamagnetic and colourless

2 Vanadium

(a) origin/occurrence X

Vanadium is the nineteenth most abundant element in the Earth's crust, with an abundance of only 0.014%. Its main ores are patronite, VS_4 , and vanadite, $\text{Pb}_3(\text{VO}_4)_2$. One potential ore-concentrating process could rely on the fact that there are some marine invertebrates that can concentrate vanadium from solution - some samples of *Ascidia Nigra* have been found to contain 1.4% of vanadium in their blood.

(b) extraction ✓

Roasting the crushed ores with sodium carbonate at $850\text{ }^{\circ}\text{C}$ produces sodium vanadate(V). The addition of sulphuric acid produces red polyvanadates, which, on heating, give black technical grade vanadium(V) oxide:



Industrially, the oxide can be reduced by aluminium in a Thermit process. The pure metal can be obtained by treating the pentachloride with hydrogen:



(c) uses

Vanadium finds its greatest use as a steel additive - it readily forms the carbide V_4C_3 with residual carbon in the steel, and this disperses in the solid matrix, forming a fine-grained steel with an increased resistance to wear and an increased high-temperature strength. World production is small, at about 4×10^4 tonnes, but production is increasing. Purified vanadium(V) oxide is widely used as the catalyst in the Contact process for making sulphuric acid.

(d) redox chemistry

Vanadium shows oxidation numbers of +5, +4, +3 and +2. The chemistry of the higher oxidation states, (V) and (IV), is complicated by a strong tendency to form a variety of different polymeric ions according to the pH of the solution. Such complications are ignored in this text; V(V) and V(IV) cations are written as $[\text{VO}_2(\text{H}_2\text{O})_4]^+(\text{aq})$ and $[\text{VO}(\text{H}_2\text{O})_5]^{2+}(\text{aq})$ respectively, these being the predominant species at low pH. The E^\ominus values quoted below allow prediction of various reactions concerning these four oxidation states.

reaction of vanadium systems	E^\ominus/V	reaction of other systems
	+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
$\text{VO}_2^+(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{VO}^{2+}(\text{aq})$	+1.00	
	+0.77	$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$
$\text{VO}^{2+}(\text{aq}) + 2\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l}) + \text{V}^{3+}(\text{aq})$	+0.34	
	+0.17	$\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l}) + \text{SO}_2(\text{aq})$
	0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26	
	-0.76	$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$
$\text{V}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{V}(\text{s})$	-1.18	

Like with titanium, metallic vanadium is much less reactive than its highly negative E^\ominus would suggest. The reason is the presence of an impervious oxide layer on its surface, as previously mentioned for other examples. The metal does, however, dissolve in aqueous acids to give, initially, solutions of the violet $\text{V}^{2+}(\text{aq})$. These are easily oxidised to the green V(III) state. The most common starting point for investigating the oxidation states of vanadium is an acidic solution of the vanadyl(V) ion, $\text{VO}_2^+(\text{aq})$. As the above table shows, solutions of iron(II) salts reduce this to the V(IV) oxidation state, whilst solutions of sulphur dioxide reduce V(V) to V(III). In order to obtain solutions of V(II), zinc metal in acidic solution is required.

Write balanced equations for the reduction of: VO_2^+ by Fe^{2+} ; VO^{2+} by SO_2 ; V^{3+} by Zn^{2+} .

Vanadium was named after Vanadis, the Scandinavian goddess of beauty, because of the large range of colours it exhibits in its complexes. To illustrate this, the colours and formulae of the important vanadium-containing aqueous ions are given in the following table, together with the colours of the anhydrous fluorides and chlorides.

oxidation state of vanadium:	V	IV	III	II
aqueous ion:	$[\text{VO}_2(\text{H}_2\text{O})_4]^+$	$[\text{VO}(\text{H}_2\text{O})_5]^{2+}$	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$	$[\text{V}(\text{H}_2\text{O})_6]^{2+}$
colour:	yellow	blue	green	violet
fluoride:	VF_5	VF_4	VF_3	VF_2
colour:	white	lime green	yellow-green	blue
chloride:		VCl_4	VCl_3	VCl_2
colour:		red-brown	red-violet	pale green

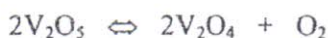
(e) complexes

All four oxidation states form octahedral complexes, examples (in addition to the aquo ions above) being $[\text{V}(\text{CN})_6]^{4-}$, $[\text{V}(\text{C}_2\text{O}_4)_3]^{3-}$, $[\text{VCl}_6]^{2-}$ and $[\text{VF}_6]^-$. Tetrahedral complexes are also common, as in $[\text{VCl}_4]^-$, VCl_4 and VOCl_3 . Vanadium(V) complexes are diamagnetic d^0 systems, whereas complexes of vanadium in the lower oxidation states are increasingly paramagnetic (V(II) has 3 unpaired d electrons).

Q Calculate the oxidation numbers of vanadium in the seven complex ions or molecules with the formulae given above.

(f) other compounds and reactions

Vanadium(V) oxide is widely used as an industrial catalyst, not only for oxidising sulphur dioxide to sulphur trioxide in the familiar Contact process for the manufacture of sulphuric acid, but also in less well known redox reactions such as the oxidation of various organic compounds by air, and the reduction of alkenes and aromatic hydrocarbons by hydrogen. The catalytic activity could well be due to solid V_2O_5 readily losing oxygen reversibly on heating, thus facilitating a change in oxidation number of the reacting compound:

**(g) summary of the chemistry of vanadium**

- main oxidation states are +2, +3, +4 and +5, the +2 state being very easily oxidised and the +4 state being the most stable
- main stereochemistry of complexes is octahedral, but tetrahedral is also important
- colours of aqueous ions are: V(II) pale violet; V(III) bright green; V(IV) "copper-sulphate" blue; V(V) yellow
- All oxidation states except V(V) are paramagnetic

3 Chromium**(a) origin/occurrence**

At a crustal abundance of 0.012%, chromium is not common, and there is only one ore, chromite, FeCr_2O_4 , of commercial importance. Over 90% of the world's reserves of chromite are located in South Africa. Other ores include crocite, PbCrO_4 , and chrome ochre, Cr_2O_3 .

(b) extraction

Reducing chromite with carbon in an electric furnace produces "ferrochrome", an iron-chromium alloy that can be used directly in stainless steels. The pure metal is made by a three-stage process involving the air oxidation of chromite in molten alkali to produce sodium chromate(VI), followed by reduction to the trioxide with carbon, and performing a Thermit reduction with aluminium:

**(c) uses**

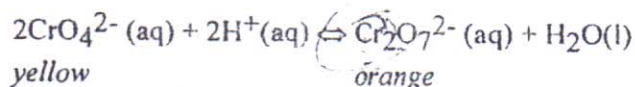
Despite its highly negative E^\ominus value, chromium is remarkably resistant to corrosion, due to the presence of a thin, hard, impervious and tenacious oxide layer. This accounts for its main uses. Most chromium is used to make stainless steels (which contain about 18% chromium) and for the chromium-plating of steel articles. This may be achieved by making them the cathode in a cell containing Cr_2O_3 dissolved in dilute sulphuric acid. World production is around 1×10^6 tonnes per year.

(d) redox chemistry

The common oxidation states of the element chromium are +2, +3 and +6. Compounds of chromium in each these oxidation states are readily prepared. E° data for the interconversion between these oxidation states given in the table below:

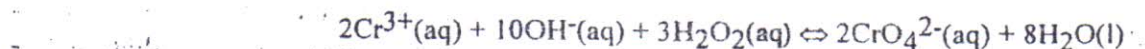
	reaction of chromium systems	E°/V	reaction of other systems
1	$\frac{1}{2}\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 7\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}^{3+}(\text{aq}) + 3\frac{1}{2}\text{H}_2\text{O}(\text{l})$	+1.33	
2		+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}$
3		+0.87	$\text{H}_2\text{O}_2(\text{aq}) + \text{OH}^-(\text{aq}) + 2\text{e}^- \rightleftharpoons 3\text{OH}^-$
4		0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
5	$\text{Cr}^{3+}(\text{aq}) + 8\text{OH}^-(\text{aq}) \rightleftharpoons \text{CrO}_4^{2-}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) + 3\text{e}^-$	-0.13	
6	$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.41	
7	$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.74	
8	$\text{Cr}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cr}(\text{s})$	-0.91	

E° values given in the above table can be used to predict that chromium metal should react with hydrogen in under standard acid conditions. Chromium does, in fact, displace hydrogen slowly from dilute hydrochloric acid and dilute sulphuric acid, being itself oxidised to $\text{Cr}^{2+}(\text{aq})$ ions. The blue $\text{Cr}^{2+}(\text{aq})$ is powerfully reducing and rapidly oxidised to $\text{Cr}^{3+}(\text{aq})$ in contact with air. Cr^{3+} is the stable cationic form of this element although Cr compounds can be prepared in the absence of water. $\text{Cr}(\text{VI})$ is the important high oxidation state of chromium and occurs in two well-known anions, the chromate(VI), CrO_4^{2-} , and the condensed - or dimeric - form, the dichromate(VI), $\text{Cr}_2\text{O}_7^{2-}$. Other more complex polymeric species also exist. The chromate(VI) ion is stable in alkaline solution, but dichromate(VI) is favoured at lower pH. The relationship is summarised by the equilibrium



The CrO_4^{2-} ion is tetrahedral, like the SO_4^{2-} and MnO_4^- ions. The $\text{Cr}_2\text{O}_7^{2-}$ ion consists of two tetrahedra joined by a common vertex (the bridging oxygen atom), having a Cr-O-Cr angle of 126° .

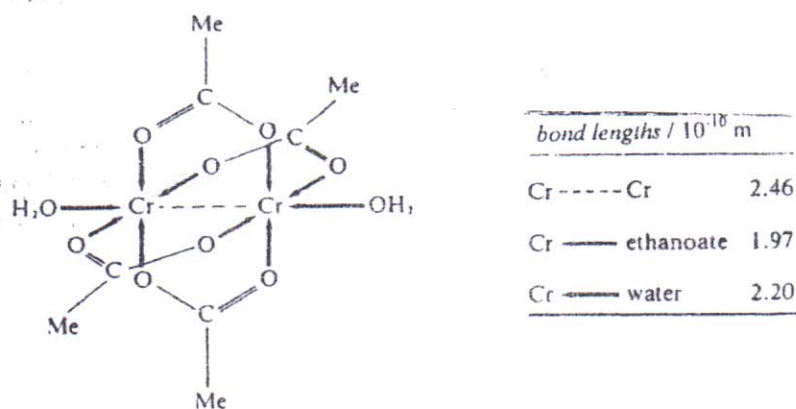
The traditional preparation of sodium dichromate(VI) from a chromium(III) compound provides a useful illustration both of the Cr(III) - Cr(VI) relationship and of the $\text{CrO}_4^{2-} \leftrightarrow \text{Cr}_2\text{O}_7^{2-}$ interconversion. As the above E° values show, a peroxide, such as hydrogen peroxide, may be used in order to oxidise Cr(III) to Cr(VI) in alkaline solution. The overall equation can be deduced from the two half equations as follows:



Removal of the excess of chromium(III) hydroxide by filtration leaves a yellow solution containing $\text{CrO}_4^{2-}(\text{aq})$ which may be converted to an orange solution of $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$ by acidifying. Dichromate(VI), like manganate(VII), is a powerful oxidant, especially in acid solution. The sodium and potassium compounds find wide application in the laboratory: in testing for reducing agents; as oxidising agents in preparative organic chemistry; and in volumetric analysis.

(e) complexes

Apart from the sky-blue octahedral $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ ion, Cr(II) also forms the interesting red insoluble ethanoate complex with the empirical formula $\text{Cr}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$. The structure is dimeric, however, with four ethanoate ions bridging across the two chromium atoms, which are in turn joined to each other by a short Cr-Cr bond. Each chromium is thus surrounded by four oxygen ligands, in a square-planar arrangement, and a fifth oxygen ligand, from a water molecule, creating an octahedral environment.

Fig. B3.1: $[\text{Cr}(\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}]_2$

In its most common oxidation state of +3, chromium forms mainly octahedral complexes, although a few tetrahedral ones, such as $[\text{CrCl}_4]^-$, are known. Cr^{3+} is the most stable of the trivalent transition metal ions and a large variety of compounds of chromium in this oxidation state have been isolated and studied. The simple aquo-ion is the violet, octahedral $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, present in solid chromium(III) potassium sulphate ('chrome alum') and in cold aqueous solutions of this compound. Warming produces a change to green, the colour most frequently shown by Cr(III) compounds. This is a result of the partial replacement of water molecules by other ligands; by sulphate ion, for instance, in the case of chrome alum. The acidity of the aquated Cr^{3+} ion is a notable feature and is a result of the high charge-to-size ratio of this ion. This behaviour is considered in more detail in connection with the ion $\text{Fe}^{3+}(\text{aq})$. Some of the more common precipitation and acid-base reactions of $\text{Cr}^{3+}(\text{aq})$ are summarised below:



Apart from illustrating the amphoteric nature of the $\text{Cr}^{3+}(\text{aq})$ ion, these reactions also demonstrate a key feature of the chemistry of Cr(III): the kinetic inertness of the ligand-metal bond. As can be seen from the above equations, all these reactions occur without the breaking of any of the Cr-O bonds. The complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is well known, but chromium(III) hydroxide dissolves in aqueous ammonia solutions only very slowly. It is this kinetic inertness which allows so many isomers to be stable.

The abundance of six-fold co-ordination complexes produces a variety of types of isomerism in transition metal compounds, which has been described in Section A8(c). Much of the original work on this used chromium(III) complexes. Compounds having the empirical formula $\text{CrCl}_2(\text{H}_2\text{O})_6$ show ionisation isomerism; the dichlorotetraamminechromium(III) cation, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, shows *cis-trans* (geometrical) isomerism; and bidentate ligands such as the ethanedioate anion and the ethane-1,2-diamine molecule form the chiral complexes $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$, neither of which has a centre or a plane of symmetry.

(f) other compounds and reactions

Sodium dichromate(VI) and potassium dichromate(VI) are the most widely used oxidising agents in organic and inorganic chemistry. They are stable orange crystalline solids and are normally used in acid solution. The deep red covalent liquid chromium(VI) oxochloride, CrO_2Cl_2 , also finds a use as an oxidising agent in organic chemistry. "Chrome yellow" is the name given to various insoluble pigments which contain the CrO_4^{2-} ion, an example being lead chromate(VI).

(g) summary of the chemistry of chromium

- main oxidation states are +2, +3, and +6, the +2 state being very easily oxidised and the +6 state being a strong oxidising agent
- main stereochemistry of complexes is octahedral, and a multitude of isomers can be made due to the kinetic inertness of the ligand-metal bond in Cr(III) complexes
- colours of aqueous ions are: Cr(II) pale blue; Cr(III) bright green; Cr(VI) orange in acidic solution, yellow in alkali
- all oxidation states except Cr(VI) are paramagnetic

4 Manganese

(a) origin/occurrence ✓

Manganese is the twelfth most abundant element in the Earth's crust, with an abundance of 0.1%. Its main ores are pyrolusite, MnO_2 , hausmannite, Mn_3O_4 and rhodochrosite, MnCO_3 . Interest has been shown in manganese "nodules", containing 20% to 30% manganese, which have been discovered on the bed of the Pacific Ocean.

(b) extraction ✓

As with chromium, most manganese is produced as a steel additive. The most commonly used form is as an alloy, "ferromanganese", containing 80% Mn and 20% Fe by mass. This is produced by reducing a mixture of MnO_2 and Fe_2O_3 with coke in a blast furnace. The pure metal may be obtained by the electrolysis of aqueous manganese(II) sulphate.

(c) uses ✓

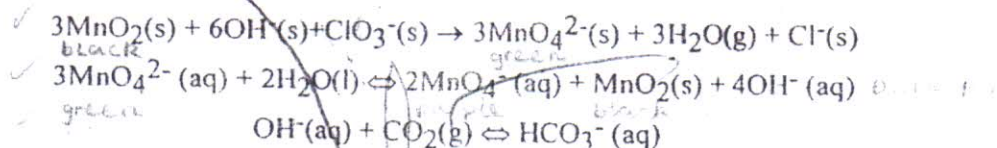
Its use as a steel additive at a small percentage relies on manganese's ability to "scavenge" residual sulphur from the steel. The MnS formed can pass into the slag, thus avoiding the brittleness of steels containing FeS. At higher percentage, it produces very hard steels, such as Hadfield (13% Mn and 1.2% C by mass).

(d) redox chemistry

Manganese shows a greater range of oxidation numbers, +1 to +7 inclusive, than any other member of the transition series. Mn(VII), Mn(IV) and Mn(II) are particularly common and important, although both Mn(VI) and Mn(III) are encountered. Redox equilibria can be set up between most pairs of oxidation states, as the following table shows:

	reaction of manganese systems	E^0/V	reaction of other systems
1	$MnO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	+2.26	
2	$MnO_4^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O(l)$	+1.67	
3	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.52	
4	$Mn^{3+}(aq) + e^- \rightleftharpoons Mn^{2+}(aq)$	+1.49	
5		+1.36	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$
6	$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23	
7		+1.23	$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$
8		+0.77	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$
9	$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.60	
10	$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59	
11	$MnO_4^-(aq) + e^- \rightleftharpoons MnO_4^{2-}(aq)$	+0.56	
12	$MnO_4^{2-}(aq) + e^- \rightleftharpoons MnO_4^{3-}(aq)$	+0.27	
13		0.00	$H^+(aq) + e^- \rightleftharpoons \frac{1}{2}H_2(g)$
14		-0.49	$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2C_2O_4(aq)$
15	$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18	

As can be seen from the table, manganese metal is highly electropositive. It liberates hydrogen from water and dilute acids, forming Mn(II) salts. Mn(VII) is present in the familiar deep-purple MnO_4^- anion. The laboratory preparation of potassium manganate(VII) involves fusing together manganese(IV) oxide, potassium hydroxide and some suitable oxidant such as potassium chlorate(V), and extracting the resulting green potassium manganate(VI) with hot water. Bubbling carbon dioxide through the boiling solution of the Mn(VI) compound aids a disproportionation reaction which gives rise to black insoluble manganese(IV) oxide and a purple aqueous solution of potassium manganate(VII).



This reaction is not only a satisfactory preparation but also an excellent demonstration of the interconversions that are possible between different oxidation states and the way in which the possibility of such changes is dependent on pH.

Another example of how the course of a redox reaction can be altered by changing the pH is given by the following.

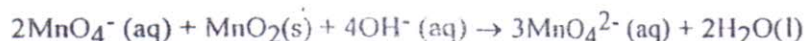
Comparison of the E° values for Mn(VI)/Mn(IV) and Mn(VII)/Mn(VI) in the above table (reactions 1 and 11) shows that the disproportionation:



is quantitative ($E^{\circ}_{\text{cell}} = +1.70 \text{ V}$) if all substances are present in their standard states. Even in standard alkaline solution (reactions 10 and 11), the disproportionation:



is still somewhat favoured ($E^{\circ}_{\text{cell}} = +0.03 \text{ V}$). However, if the solution is made strongly alkaline, the green manganate(VI) ion is stabilised. This occurs during the preparation previously described and may be confirmed by shaking together a solution of potassium manganate(VII), some manganese(IV) oxide and some pellets of potassium hydroxide. Increasing the concentration of one of the species, OH^- , in the reduced form of the Mn(VI)/Mn(IV) equilibrium makes the combination less strongly oxidising, and the E° value can fall below that of the Mn(VII)/Mn(VI) reaction. The effect is particularly marked in this case, since the value of the potential depends on the term $[\text{OH}^-]^4$. Under these conditions, the direction of spontaneous change is reversed and the favoured reaction is now:



In Le Chatelier terms, raising the concentration of hydroxide ion causes more manganate(VII) ions and manganese(IV) oxide to react, giving rise to more manganate(VI) ions.

Potassium manganate(VII) is perhaps the most familiar of all the common oxidants. It is particularly effective in acid solution, as there is a very strong pH-dependence, the electrode potential depending on the eighth power of the hydrogen ion concentration, i.e. $E^{\circ} \propto [\text{H}^+]^8$. The widespread use of potassium manganate(VII) as an oxidising agent in diagnostic testing, in preparative work and in quantitative analysis is well-known. As the above E° values suggest;

- it oxidises $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$ quantitatively,
- it oxidises ethanedioate, $\text{C}_2\text{O}_4^{2-}(\text{aq})$, to $\text{CO}_2(\text{g})$ quantitatively,
- it is an excellent oxidising agent for the laboratory preparation of chlorine from concentrated (10 mol dm^{-3}) hydrochloric acid.

Q: Calculate E°_{cell} for the first two of these reactions, and write equations for all three of them, using an acidic solution of $\text{MnO}_4^-(\text{aq})$.

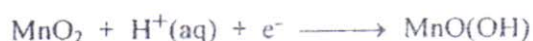
(e) complexes

The stable cationic state of manganese present in solid manganese(II) salts and in aqueous solution is the pale-pink octahedral ion $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$. This intensely paramagnetic ion contains 5 unpaired d electrons, one in each orbital. The reasons for its extremely pale colour have already been explained in section A6. Mn(II) forms rather fewer complexes in aqueous solution than most of the cations in this first transition series; for instance, it forms neither an ammine nor a hydroxo complex, possibly due to its high kinetic instability/reactivity (in contrast to Cr(III), for example). Green-yellow complexes containing tetrahedral ions such as $[\text{MnCl}_4]^{2-}$ are also known. Octahedral complexes are formed by Mn(III) (e.g. the dark red $[\text{Mn}(\text{CN})_6]^{3-}$) and by Mn(IV) (e.g. $[\text{MnF}_6]^{2-}$), but the higher oxidation states exist only as the tetrahedral oxoanions MnO_4^{3-} , MnO_4^{2-} and MnO_4^- .

(f) other compounds and reactions

One important and distinctive reaction of $\text{Mn}^{2+}(\text{aq})$ ions occurs with aqueous alkali. Both aqueous sodium hydroxide and aqueous ammonia will precipitate white manganese(II) hydroxide. This precipitate will not dissolve in an excess of either reagent, but it does become brown on standing in contact with air. The colour change is attributed to the formation of $\text{Mn}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, a brown hydrated manganese(III) oxide.

Manganese(IV) oxide is the only common and useful manganese(IV) compound. Its most important reactions involve its oxidising ability. It is able to oxidise, for example, concentrated hydrochloric acid (on warming), ethanedioates and iron(II) salts. It is also a useful catalyst, capable of accelerating the release of oxygen from oxygen-rich compounds such as hydrogen peroxide and potassium chlorate(V). Industrially, a large tonnage of MnO_2 goes into the manufacture of dry-cell batteries, where it acts as a depolariser, to prevent the production of hydrogen at the positive electrode, which could cause a dangerous build-up in pressure. The depolarising reaction involves its reduction to Mn(III):



(g) summary of the chemistry of manganese

- main oxidation states are +2, +4, and +7, but +3, +5 and +6 states are also known
- although intermediate oxidation states are often unstable through disproportionation, they are normally obtainable, under conditions of extreme pH
- complexes are only formed by the +2, +3 and +4 oxidation states: their main stereochemistry is octahedral, but a few tetrahedral complexes are also known
- colours of aqueous ions are: $\text{Mn}^{2+}(\text{aq})$ pale pink; $\text{Mn}^{3+}(\text{aq})$ red; $\text{MnO}_4^{3-}(\text{aq})$ bright blue; $\text{MnO}_4^{2-}(\text{aq})$ green; $\text{MnO}_4^{-}(\text{aq})$ deep purple
- all oxidation states except Mn(VII) are paramagnetic

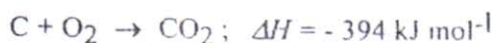
5 Iron

(a) origin/occurrence ✓

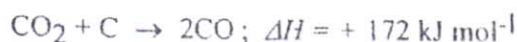
At 6.2% of the Earth's crust, iron is the fourth most abundant element. Its main ores are: haematite, Fe_2O_3 ; magnetite, Fe_3O_4 ; limonite, $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$; and siderite, FeCO_3 .

(b) extraction ✓

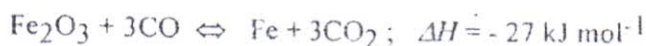
The reduction of iron ores to pig iron in the Blast Furnace is well known. The raw materials are iron ore (e.g. haematite), coke, limestone and air. The solid materials are fed in at the top of the furnace while air enters near the base, reacting exothermically with coke to form carbon dioxide.



On passing up the furnace, the hot carbon dioxide is reduced by reacting with more coke in an endothermic process.



Reduction of the iron ore by carbon monoxide, which is an exothermic reaction, occurs in the upper part of the furnace which is cooler.

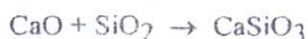


The molten iron produced then falls to the bottom of the furnace.

The function of the limestone is to remove impurities, such as silica, in the form of a slag. The high temperature causes the calcium carbonate to decompose to calcium oxide and carbon dioxide.



Silica, being an acidic oxide, reacts with the basic calcium oxide to form molten calcium silicate (slag).



As molten iron has a much higher density than slag, two layers are formed at the base of the furnace and they can be tapped off separately.

Pure iron can be obtained on the small scale by reducing its oxides or hydroxides with hydrogen, or by making its pentacarbonyl and decomposing this at a high temperature (compare the process for nickel, see Section B7(b)):



(c) uses

The uses of steel need no introduction. It is by far the more common metallic construction material, with 7×10^8 tonnes being produced per year. Railway rails, car bodies, washing machines, girders for offices and bridges - all require steels of slightly different properties to be manufactured on the millions of tonne scale. Pig iron has its own uses too, and 5×10^8 tonnes per year are used where a harder (but more brittle) metal is required.

(d) redox chemistry

Iron shows very few oxidation states in its common compounds: Fe(II) and Fe(III) are well known, Fe(VI) occurs only as the deep red, strongly oxidising, tetrahedral ferrate anion, FeO_4^{2-} . Even less characterised is the FeO_4^{3-} ion, the sole representative of Fe(V). The redox chemistry of the Fe(II)-Fe(III) system has been exhaustively studied, however, including the influence of ligand on the redox potential.

reaction of iron systems	E^0/V	reaction of other systems
$\text{FeO}_4^{2-}(\text{aq}) + 8\text{H}^+(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	+2.20	
	+1.52	$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$
	+1.36	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$
	+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	+0.77	
	+0.54	$\frac{1}{2}\text{I}_2(\text{aq}) + \text{e}^- \rightleftharpoons \text{I}^-(\text{aq})$
	+0.40	$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$
$[\text{Fe}(\text{CN})_6]^{3-}(\text{aq}) + \text{e}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}(\text{aq})$	+0.36	
	0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44	
$\text{Fe}(\text{OH})_3(\text{s}) + \text{e}^- \rightleftharpoons \text{Fe}(\text{OH})_2(\text{s}) + \text{OH}^-(\text{aq})$	-0.56	

As predicted from its negative E° value, iron dissolves steadily in dilute acids to produce solutions of iron(II) salts. Iron has no reaction with air, oxygen or water separately at room temperature, but when present together, rusting readily occurs. This type of behaviour, which is shown by most of the elements in the first transition series, demonstrates once again the primacy of kinetic considerations and the danger of basing predictions on E° values alone.

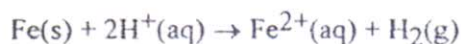
Iron filings "sparkle" when heated in air or oxygen:



and hot iron reduces steam in a frequently-cited example of a heterogeneous reversible reaction.

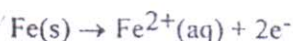


Hydrochloric acid and sulphuric acid, when hot and dilute, each oxidise iron to Fe^{2+} (aq) moderately quickly.

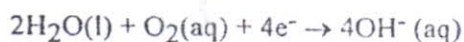


Dilute nitric acid produces Fe^{3+} (aq), while concentrated nitric acid renders the metal passive.

The corrosion of iron by the destructive process of rusting is essentially electrochemical in nature. The surface of a piece of iron, however smooth and pure, is not electrochemically homogeneous. Effects such as scratching, deformation and, in particular, differential aeration, produce sites of inhomogeneity. In the anodic areas (see Fig. B5.1), the reaction is:



In the cathodic regions, however, the following reaction occurs:



The result is the formation of large numbers of small cells. If the water contains ions from other dissolved electrolytes, such as carbonic acid or sodium chloride, the resulting increased conductivity of the water accelerates the corrosion process. Close proximity of anodic and cathodic regions will allow the precipitation of iron(II) hydroxide and, in the presence of further oxygen, the formation of the complex iron(III) compound usually described as hydrated iron(III) oxide, known as rust.

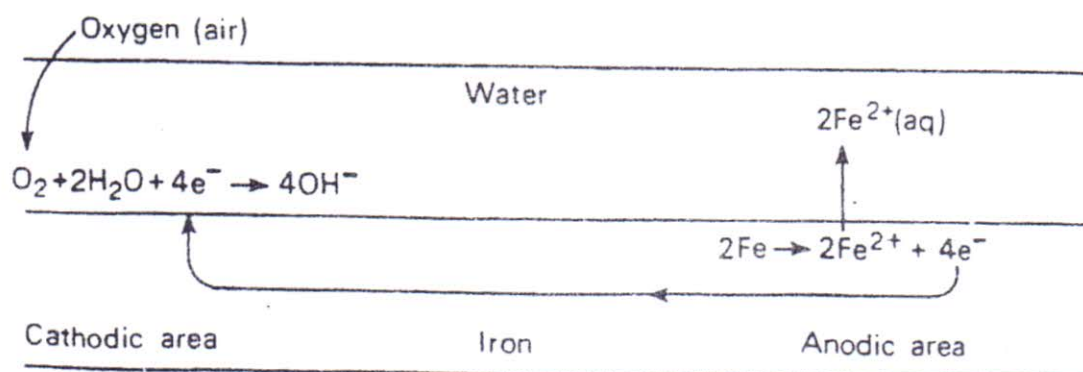
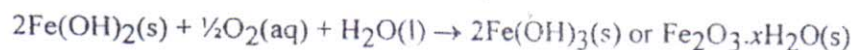


Fig B5.1: Rusting of iron in contact with water

Examination of the equation for the cathodic couple shows why corrosion is more severe at points remote from the air as, for example, inside the box sections of a motor-car. A lower concentration of oxygen means that the reduction of oxygen molecules to $\text{OH}^-(\text{aq})$ occurs less readily; that is, an oxygen-poor region is more anodic with respect to regions where a higher concentration of oxygen exists, such as at a surface freely exposed to the atmosphere. The ionisation of iron atoms, therefore, is the preferred change in places remote from oxygen, and such places are sites for the onset of the rusting process, the further oxidation of $\text{Fe}^{2+}(\text{aq})$ to $\text{Fe}^{3+}(\text{aq})$ occurring where oxygen is available.

A variety of methods is used in an effort to combat the ravages of the rusting process. These include coating alloying, cathodic protection and inhibition as described below.

- Coating the iron and steel surface sets up a barrier between the surface and the corroding agents, water and oxygen. Such surface protection is achieved in a number of different ways; painting and coating with another metal are commonly used on iron and steel surfaces. Zinc coating, i.e. galvanising, is particularly effective. If a scratch exposes the iron surface beneath, the more electropositive zinc, not the iron corrodes. Paint containing phosphoric(V) acid may also be used. This forms a layer of insoluble iron(III) phosphate with any rust already present on the surface.
- Alloying - chromium is incorporated in stainless steel; its corrosion resistance being due to the production of an impervious surface-oxide film.
- Cathodic protection is commonly achieved by connecting the iron to a block of a more electropositive metal, usually zinc or magnesium. The anodic process is now the "sacrificial corrosion" of the zinc or magnesium so that the iron remains unaffected (see Fig. B5.2). An alternative approach uses an external e.m.f. in which an inert conducting material, e.g. graphite, is connected to the positive side of a battery with the negative side being connected to the iron to be protected. The negative potential acquired by the iron inhibits the formation of Fe^{2+} ions.

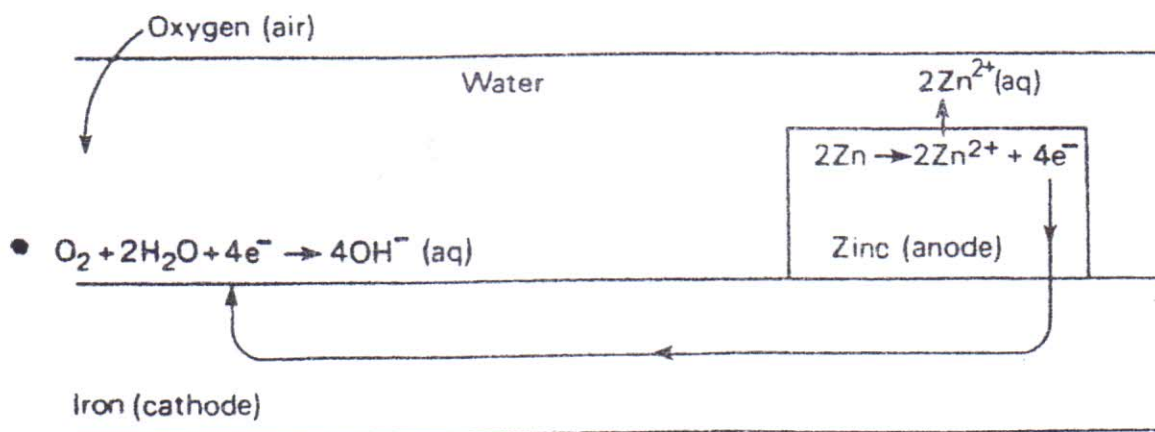
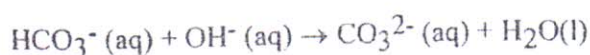


Fig B5.2

- Both anodic and cathodic inhibitors exist, although it is claimed that the latter type is generally more effective. Hydrogencarbonate ions, for instance, remove OH^- ions from the vicinity of the cathode and cause the formation of an insoluble carbonate, thereby denying the oxygen access to the surface.



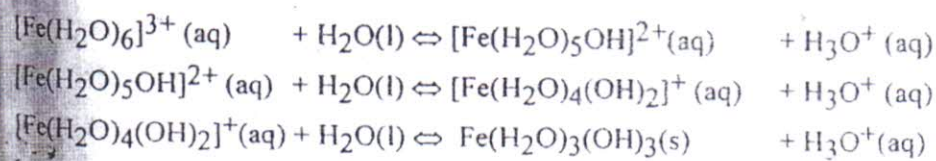
A large number of simple interconversion reactions involving iron(II) and iron(III) compounds is possible. Oxidants such as $\text{MnO}_4^-/\text{H}^+$, bromine and nitric acid, and reductants such as Zn/H^+ , hydrogen sulphide and iodide ions, can readily effect the change. The E° value, and hence the relative stability of $\text{Fe}^{3+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$, is affected by changes in the pH of the medium, as can be seen from reactions 5 and 11 in the above table. The iron(II) state is much more strongly reducing in alkaline solution. This may be explained in terms of the easier removal of an electron from the uncharged $\text{Fe}(\text{OH})_2$, as opposed to the positively charged Fe^{2+} . It is common practice to make up iron(II) salt solutions in acidic solution in order to stabilise them with respect to oxidation. However, reference to the E° values for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and the oxygen systems (reactions 4 and 7 in the table) shows that this stabilisation must be due to kinetic factors: The standard cell potential for the oxidation ($E^\circ_4 - E^\circ_5$) is +0.46 V even in acidic conditions, so that oxidation would still be effectively complete.

A further interesting example of change in the relative stability of oxidation states is seen with respect to the cyanide ligand. The E° value shows that a considerable stabilisation of iron(III) with respect to iron(II) occurs. A simple and effective investigation of this change can be made using the iodine/iodide ion system, where colour changes are easily seen.

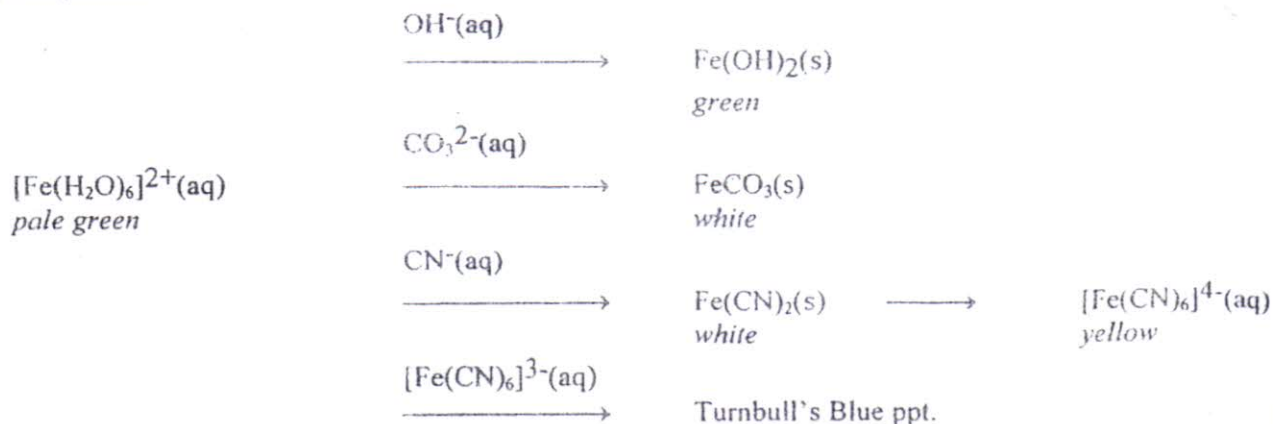
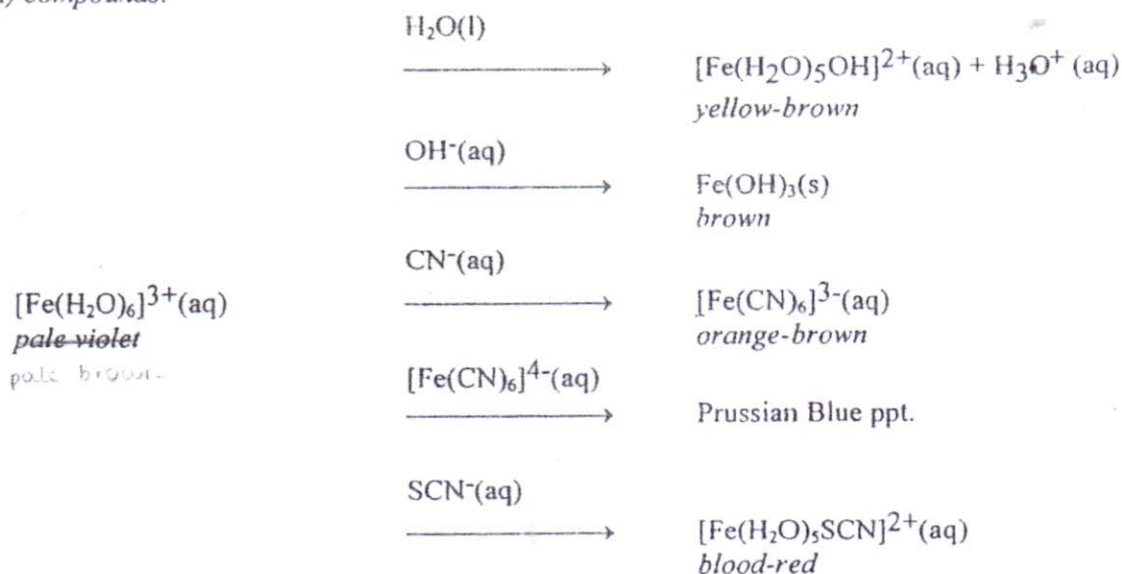
Thus, using reactions 5 and 6, it can be predicted that Fe^{3+} can oxidise I^- to iodine, but from reactions 6 and 8 it can be predicted that $[\text{Fe}(\text{CN})_6]^{3-}$ is unable to do so. Indeed, $[\text{Fe}(\text{CN})_6]^{4-}$ should decolourise iodine solution. Such predictions are observed in practice.

(e) complexes

The predominant geometry of iron(II) and iron(III) complexes is octahedral, although the tetrahedral FeCl_4^{2-} and FeCl_4^- ions exist. The simple aquated iron(II) and iron(III) ions are the pale-green $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and the very pale violet $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$. The latter is present in solid ammonium iron(III) sulphate ('iron(III) alum'), but seldom appears in aqueous solution because ligand replacement effects occur, giving an ion which is usually yellow-brown in colour. The important acidity effect associated with co-ordinated water is well illustrated in iron chemistry. The less polarising Fe^{2+} does not produce appreciable acidity in $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$. For instance, magnesium is not attacked and iron(II) carbonate is precipitated on addition of aqueous sodium carbonate. The $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ion, by contrast, is a stronger acid than methanoic acid, the enhanced acidity being attributed to the more powerful electron attracting character of the smaller and more highly charged Fe^{3+} ion. The reactions of the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ (as well as those of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$) with reactive metals, carbonate ions, sulphide ions and hydroxide ions can be understood by reference to equilibria of the type:



The addition of basic species, such as carbonate ions, removes hydronium ions from the right-hand side of these equilibria, thereby causing the precipitation of iron(III) hydroxide, not iron(III) carbonate. In fact, salts of highly polarisable anions, such as carbonate and iodide, are not formed by iron in its oxidation state (III). Some of the more important precipitation and ligand replacement reactions of iron(II) and iron(III) compounds are summarised in the two reaction schemes below. In many cases, it is the practical diagnostic aspect of the reaction which is of interest. Simplified, inaccurate formulations such as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are therefore considered acceptable.

Iron(II) compounds:**Iron(III) compounds:**

X-ray powder patterns and other physical methods have determined that, in their pure forms, Turnbull's Blue and Prussian Blue are identical, with the formula $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 15\text{H}_2\text{O}$, and a structure that is best described as a cubic lattice of Fe^{2+} and Fe^{3+} ions, with CN ligands along the cube edges, and water molecules within each cube. The formation of the blood-red thiocyanato complex is an extremely sensitive test for $\text{Fe}^{3+}(\text{aq})$ ions. Further substitution of water ligands by SCN^- ions results in $\text{Fe}(\text{SCN})_3$, $[\text{Fe}(\text{SCN})_4]^-$ and $[\text{Fe}(\text{SCN})_6]^{3-}$. Fe(III) also forms strong complexes with the F^- ion, the colourless $[\text{FeF}_3(\text{H}_2\text{O})]^{2-}$ being the predominant species in aqueous solutions of fluorides. Bidentate ligands such as ethanedioate, $\text{C}_2\text{O}_4^{2-}$, form potentially chiral octahedral complex ions such as $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$.

Q: Use the stability constants in Table 8 to predict what reaction occurs when a solution of $\text{Fe}^{3+}(\text{aq})$ is added to a solution containing F^- ions and SCN^- ions, both at the same concentration.

Unlike Fe(III), Fe(II) forms reasonably stable complexes with ammonia, e.g. $[\text{Fe}(\text{NH}_3)_6]^{2+}$. Another important compound of Fe(II) is the nitrosyl complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$, which is responsible for the colour of the "brown ring" test for the presence of nitrate ions.

(f) other compounds and reactions

Iron(III) sulphate finds an important application as a mordant in dyeing processes and as a coagulant in the treatment of drinking water and effluents of various kinds. Iron(II) sulphate and other Fe(II) salts of organic acids are components of iron supplement pills used to help cure anaemia.

The body of an adult contains about 4 g of iron, 75% of which is in the form of haemoglobin. This vital oxygen-carrying constituent of the blood contains iron in oxidation state (II). The iron atom, which is part of an immensely complex giant molecule, exhibits hexaco-ordination. Five of the co-ordination sites are occupied by nitrogen, four from a ring system and the fifth from a protein. The oxygen molecule may become reversibly bonded at the sixth site allowing the haemoglobin to carry oxygen from one part of the body to another. Ligands such as cyanide and carbon monoxide are strongly and irreversibly adsorbed at this site, and this accounts for their toxic nature. Other biologically important iron compounds are myoglobin (the oxygen transporter in muscles) and the cytochromes, which are electron transfer agents in the mitochondria. Both are based on the same iron-containing haem units.

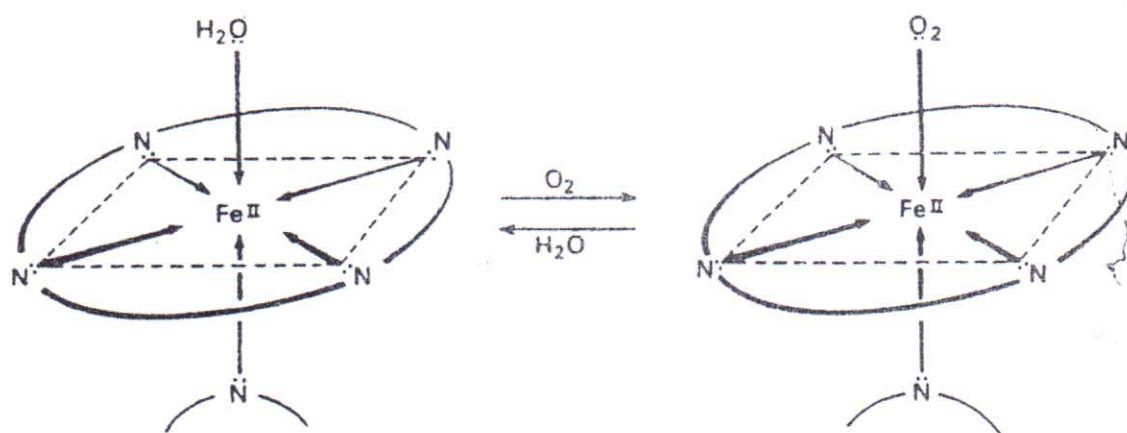


Fig B5.3: Haem

(g) summary of the chemistry of iron

- main oxidation states are +2, +3, and +6, the last being strongly oxidising
- $\text{Fe}^{3+}(\text{aq})$ ions are quite strongly acidic, being "hydrolysed" by water
- main stereochemistry of complexes is octahedral, but a few tetrahedral complexes are also known
- rusting is a redox process occurring because iron is seldom electrochemically "pure"
- all oxidation states are paramagnetic, except some "low spin" complexes of Fe(II) (see Section A4)
- iron is important biologically in the form of haemoglobin and other haem-containing complexes

(a) origin/occurrence

Cobalt is fairly rare, comprising only 0.003% of the Earth's crust. As is more common with metals to the right of the transition group, its common ores are sulphides and arsenides: smaltite, CoAs_2 ; cobaltite, CoAsS ; and linnacite, Co_3S_4 .

(b) extraction

Cobalt ores are usually mined along with ores of copper, nickel or lead. The ores are roasted to give the oxides, which are then leached with dilute sulphuric acid. Adding sodium chlorate(I) to the resulting solution of CoSO_4 precipitates Co(OH)_3 . This is dehydrated by heating, and the oxide so formed is reduced by charcoal to the metal.

(c) uses

Out of a total annual production of 3×10^4 tonnes, about 30% is used in the manufacture of high temperature alloys for gas turbines and 20% is used in magnetic alloys such as ALNICO, a steel containing aluminium, nickel and cobalt in addition to iron. This material can be fabricated into permanent magnets 25 times more powerful than ordinary steel magnets. About 30% of the production of cobalt ores goes not in the reduction to the metal but towards the manufacture of various coloured pigments in the paints and ceramics industries.

(d) redox chemistry

Cobalt seldom occurs in any oxidation state higher than (III). The common states for this element are (II) and (III), the former being by far the more stable in normal aqueous conditions. The E^\ominus values quoted below show how the oxidising power of Co(III) is diminished when ligands other than water surround the central ion:

	reaction of cobalt systems	E^\ominus/V	reaction of other systems
1	$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + e^- \rightleftharpoons [\text{Co}(\text{H}_2\text{O})_6]^{2+}$	+1.81	
2		+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
3	$[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-} + e^- \rightleftharpoons [\text{Co}(\text{C}_2\text{O}_4)_3]^{4-}$	+0.57	
4	•	+0.40	$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2e^- \rightleftharpoons 2\text{OH}^-(\text{aq})$
5	$\text{CoO(OH)}(\text{s}) + e^- \rightleftharpoons \text{Co(OH)}_2(\text{s})$	+0.17	
6	$[\text{Co}(\text{NH}_3)_6]^{3+} + e^- \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{2+}$	+0.11	
7		0.00	$\text{H}^+(\text{aq}) + e^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
8	$\text{Co}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Co}(\text{s})$	-0.29	
9	$[\text{Co}(\text{CN})_6]^{3-} + e^- \rightleftharpoons [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-} + \text{CN}^-(\text{aq})$	-0.80	

Simple cobalt(III) compounds, such as cobalt(III) fluoride, may be prepared under anhydrous conditions but such compounds liberate oxygen from water as would be predicted from E^\ominus values. On the other hand, complexes involving ammonia and cyanide ions are prone to ready oxidation by air and have to be kept under a nitrogen atmosphere.

Q: Write a balanced equation, and calculate E^\ominus_{cell} , for the reaction between Co^{3+} and acidified water.

Thus, the addition of aqueous ammonia to an aqueous solution of a cobalt(II) salt gives a blue precipitate of cobalt(II) hydroxide. If left in the air, this is oxidised to cobalt(III) "hydroxide" (reaction 5 in the above table). Cobalt(II) hydroxide dissolves in an excess of aqueous ammonia to form a pale brown solution which is oxidised on contact with air to give a darker brown solution containing Co(III) (reaction 6 in the above table).

(e) complexes

As is the case with chromium, the ligand-metal bond in the +3 oxidation state of cobalt is kinetically inert, whereas in the +2 state it can easily be replaced. This fact, coupled with the ease of oxidation of *complexed* Co(II), was made use of in the preparation of many classic Co(III) complexes at the end of the 19th Century. Thus, if a ligand of choice is added to an aqueous solution of a cobalt(II) salt, and the cobalt(II) complex formed is oxidised by either hydrogen peroxide or by air in the presence of activated charcoal. Using this method, a variety of cobaltammines have been prepared, which show all the classic isomerism to be expected from kinetically inert octahedral complexes, and which demonstrate a variety of colours:

complex ion	colour
$[\text{Co}(\text{NH}_3)_6]^{3+}$	golden-brown
$[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+}$	bright red
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	purple
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (<i>cis</i>)	deep violet
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ (<i>trans</i>)	green

Apart from the fluoro complex $[\text{CoF}_6]^{3-}$, all Co(III) complexes are "low spin", having their six d electrons paired in the three lower energy d orbitals; they are, accordingly, diamagnetic.

The more familiar cobalt(II) state also forms many complexes. In general, these are either pink and octahedral or blue and tetrahedral. A simple test-tube investigation using a pink aqueous solution of cobalt(II) chloride provides an excellent illustration of this relationship. The change to blue may be achieved either by heating or by adding concentrated hydrochloric acid.

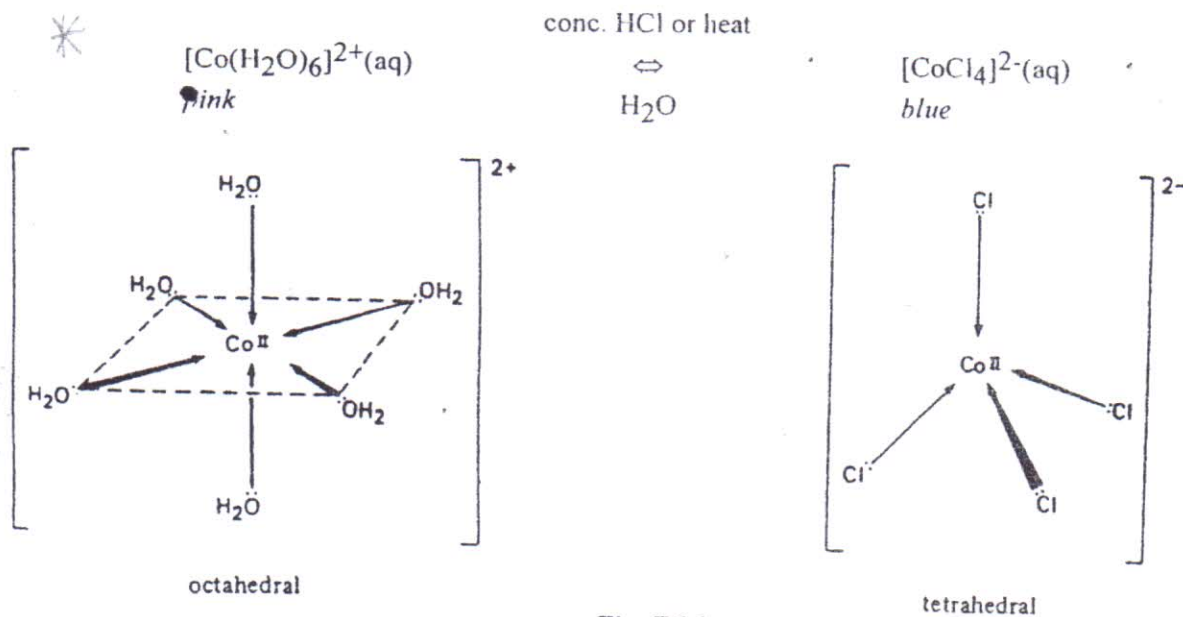


Fig. B6.1

Addition of water to the blue solution produces a new equilibrium mixture in which the pink species predominates.

(f) other compounds and reactions

Pernicious anaemia involves faulty development of the red blood corpuscles and is a result of the liver being unable to supply a substance needed for the formation of red cells. This missing substance is a cobalt compound, vitamin B₁₂. This immensely complex molecule contains hexaco-ordinate Co(III). There are four donor nitrogen atoms from a ring system. The fifth donor atom, also nitrogen, is part of another ring system. The sixth donor is a carbon atom of a sugar group. The ligand at this co-ordination site can be readily replaced and the vitamin is often isolated in a form called cyanocobalamin, in which the cyanide group occupies this position.

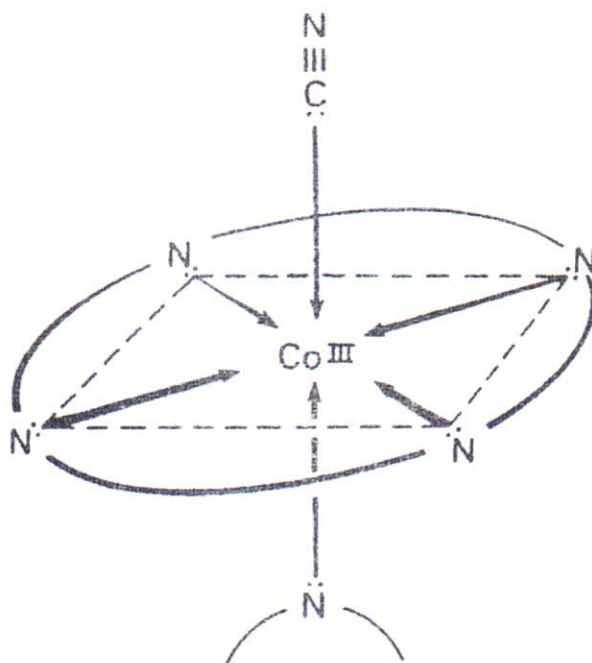


Fig B6.2: Schematic representation of cyanocobalamin

Most biochemical reactions with enzymes which use B₁₂ as a cofactor are rearrangements involving the exchange of a hydrogen atom and another group from one carbon atom to an adjacent one:



Despite its importance in the synthesis of various key chemicals in the formation of essential cells in the organism, vitamin B₁₂ is needed in only microgram quantities. The average human body contains less than 5 mg, in the liver.

(g) summary of the chemistry of cobalt

- main oxidation states are +2, and +3
- Co³⁺(aq) ions are strongly oxidising, but complexed Co(III) is stable
- main stereochemistry of complexes is octahedral, but a few tetrahedral complexes are also known
- Co(II) complexes are paramagnetic, whereas most Co(III) complexes are diamagnetic
- cobalt is important biologically in the form of vitamin B₁₂

7 Nickel

(a) origin/occurrence

Nickel is not a plentiful element, comprising 0.01% of the Earth's crust (although much more is believed to be a major component of the Earth's core). It occurs in complex oxides of nickel, magnesium and silicon known as laterites, and as sulphides such as pentlandites, $(\text{NiFe})_9\text{S}_8$ and NiCuS_2 .

(b) * extraction

Roasting the sulphide ores gives the oxide, which is either used directly in steelmaking, or converted into metallic nickel by reduction with carbon and refined, either electrolytically, or by the Mond process. This is still essentially the same process as was developed in Clydach, Wales in 1899. Purification is effected by heating the crude nickel with carbon monoxide at about 60 °C, forming volatile tetracarbonylnickel(0), which is distilled out. Subsequent decomposition of this compound at about 200 °C gives a very pure sample of nickel.



The alternative electrolytic process is very similar to that employed in the purification of copper: it involves casting the impure nickel into anodes and using NiCl_2 or NiSO_4 as electrolyte. The nickel deposited on the cathodes is >99.9% pure.

(c) uses ✓

Nickel is a hard, high-melting and relatively unreactive material. It is a valuable component of stainless steels, magnetic steels, "nickel silver" (20% Ni, 60% Cu and 20% Zn, by mass) and cupronickel alloy to make "silver" coins (80% Cu and 20% Ni). Nichrome (40% Cr and 60% Ni) is an important alloy for resistance wire. World production is approximately 8×10^5 tonnes per year.

It is used as an industrial catalyst, usually in the form of finely divided metal produced by reducing nickel oxide. This catalyst is used in the manufacture of Syngas (hydrogen + carbon monoxide) and also in the hydrogenation of fats (margarine manufacture).

(d) redox chemistry

At this point in the Periodic Table, near the end of the first transition series, oxidation state(II) is now considerably more stable than (III). Ni(II) is, in fact, the only stable oxidation state of this element in aqueous solution. Redox relationships are thus relatively unimportant.

	reaction of nickel systems	E^0/V	reaction of other systems
1		+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
2	$\text{Ni(OH)}_3(\text{s}) + \text{e}^- \rightleftharpoons \text{Ni(OH)}_2(\text{s}) + \text{OH}^-(\text{aq})$	+0.48	
3		+0.40	$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$
4		0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$
5	$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.25	
6	$[\text{Ni(CN)}_4]^{2-}(\text{aq}) + \text{e}^- \rightleftharpoons [\text{Ni(CN)}_3]^{2-}(\text{aq}) + \text{CN}^-(\text{aq})$	-0.40	

Nickel dissolves in dilute acids, liberating hydrogen. Reaction 2 in the table occurs in the nickel-cadmium rechargeable battery. Reaction 6 shows how complexing with a cyanide ligand can allow the formation of a low oxidation state (Ni(I)).

(e) complexes

Nickel forms a wide range of complexes. The nickel(II) ion in aqueous solution is green, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. As well as the usual octahedral complexes, 4-coordination, especially the square planar geometry, is particularly important in nickel complexes.

complex	geometry	colour
$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	octahedral	green
$[\text{Ni}(\text{NH}_3)_6]^{2+}$	octahedral	blue
$[\text{Ni}(\text{CN})_4]^{2-}$	square planar	yellow
$[\text{NiCl}_4]^{2-}$	tetrahedral	blue

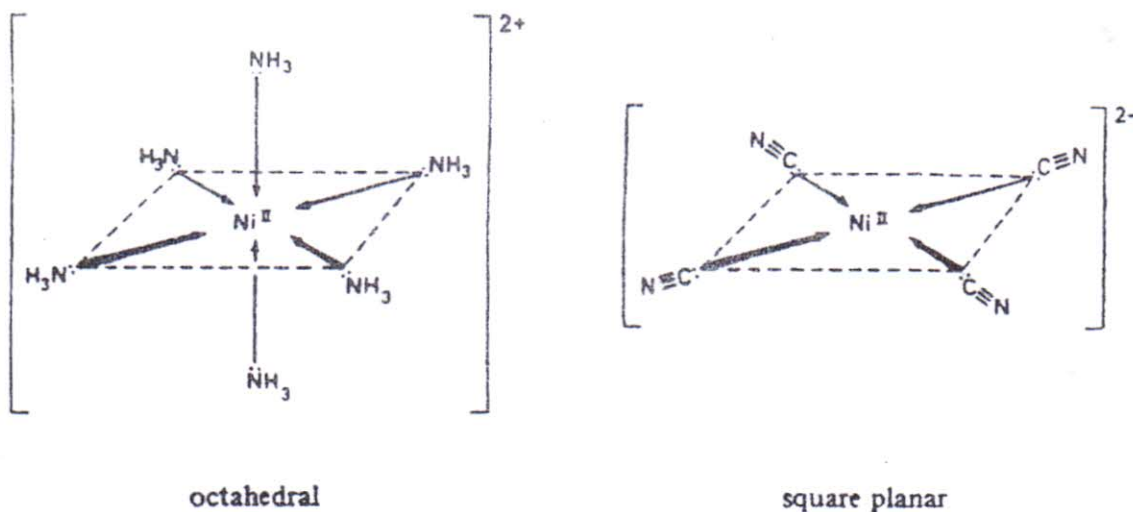


Fig B7.1

(f) other compounds and reactions

Mention should be made of the mixed oxide/hydroxides of Ni(III)/Ni(II) in the nickel-cadmium cell. The reaction occurring at the cadmium electrode is:



When the cell is being charged, electrons pumped into the cadmium electrode reduce Cd(II) to Cd, whilst at the nickel electrode Ni(II) is oxidised to Ni(III). During discharge, the reverse reactions take place.

Q: Construct a balanced equation for the overall reaction occurring during the charging process. If the overall E^\ominus_{cell} is 1.1 V under standard conditions, calculate the E^\ominus of the $\text{Cd}(\text{OH})_2/\text{Cd}$ couple.

An excellent test for the presence of nickel ions in aqueous solution is the formation of the bright red insoluble complex formed with dimethylglyoxime. This is of a square planar geometry.

(g) summary of the chemistry of nickel

- main oxidation state is +2
- stereochemistry of complexes is octahedral or square planar but a few tetrahedral complexes are also known
- octahedral complexes are paramagnetic, whereas square planar complexes are diamagnetic

8 Copper

(a) origin/occurrence

The ease of extraction and commonality of copper belies its low crustal abundance (0.007%). It occurs mainly as the sulphide ores chalcopyrite, CuFeS_2 , and chalcocite, Cu_2S . Other important sources are cuprite, Cu_2O , and malachite, $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$.

(b) extraction

The extraction of copper from "clean" sulphide ores, not containing other metals, is relatively straightforward: roasting in air causes partial oxidation to the oxide, which then undergoes an internal redox reaction to give "blister" copper.



Further purification is effected by an electrolysis treatment similar to that of nickel: the cathodic copper so formed is >99.9% pure.

If the ore contains iron sulphide too, the process is somewhat more complicated but is essentially similar in its chemistry.

(c) uses ✓

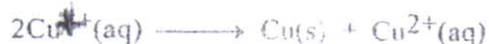
The chemical inertness and ductility of copper are responsible for its use in domestic water and gas pipework, whilst these two properties along with its high electrical conductivity explain its demand as an electrical conductor. Important alloys include the cupronickel "silver" coinage alloy, the bronzes ($\text{Cu} + 10\% \text{Sn}$) and the brasses ($\text{Cu} + \text{Zn}$). Annual production of new copper exceeds 8×10^8 tonnes.

(d) redox chemistry ✓

Copper shows two important oxidation numbers, +1 in copper(I) compounds (d^{10} configuration) and +2 in copper(II) compounds (d^9 configuration). Most copper(I) compounds are white and diamagnetic in the solid state, as expected from the d^{10} configuration. Hydrated copper(II) salts are paramagnetic; they are usually blue-green in the solid state and blue in dilute aqueous solution, the blue colour being attributed to the ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

	reaction of copper systems	E^0/V	reaction of other systems
1		+1.23	$\frac{1}{2}\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}(\text{l})$
2	$\text{Cu}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.52	
3		+0.40	$\frac{1}{2}\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons 2\text{OH}^-(\text{aq})$
4	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	+0.34	
5	$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}^+(\text{aq})$	+0.15	
6		0.00	$\text{H}^+(\text{aq}) + \text{e}^- \rightleftharpoons \frac{1}{2}\text{H}_2(\text{g})$

The above E^0 values show that copper(I) salts are unstable in aqueous solution: $\text{Cu}^+(\text{aq})$ can undergo a disproportionation reaction (reactions 2 and 5 in the table) in which one ion oxidises another:



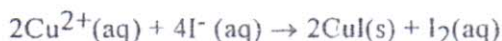
Thus, adding white Cu_2SO_4 to water produces not the colourless solution expected, but a blue solution of $\text{CuSO}_4(\text{aq})$ and a red-brown precipitate of copper metal. The equilibrium constant for the disproportionation reaction

$$K = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2} = 10^6 \text{ mol}^{-1} \text{ dm}^3$$

shows that reaction is virtually complete.

A comparison of the E^\ominus values quoted suggests that $\text{Cu}^+(\text{aq})$ might be stabilised with respect to $\text{Cu}^{2+}(\text{aq})$ and $\text{Cu}(\text{s})$ if the concentration of $\text{Cu}^+(\text{aq})$ could be reduced to a value so low that the order of the E^\ominus values previously quoted became reversed. In equilibrium terms, this means that $\text{Cu}^+(\text{aq})$ ions are removed from the disproportionation equilibrium mixture, causing $\text{Cu}(\text{s})$ to reduce Cu^{2+} , thereby producing more $\text{Cu}^+(\text{aq})$. Such a reduction in $\text{Cu}^+(\text{aq})$ concentration commonly occurs in one of the following ways.

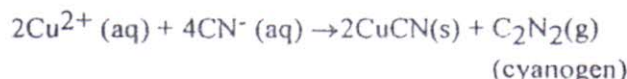
- (a) The copper(I) compound, which may be predominantly covalent, is of very low solubility. Well known examples of this are copper(I) chloride, copper(I) iodide and copper(I) cyanide. In fact, such is the insolubility of copper(I) iodide that it is precipitated when aqueous iodide ions are added to an aqueous solution of a copper (II) salt. Half the total number of iodide ions are precipitated as white copper(I) iodide, whilst the other half, which have been responsible for the reduction of the $\text{Cu}^{2+}(\text{aq})$ ions, are oxidised to iodine.



This reaction, coupled with the titration of the iodine formed using standardised aqueous sodium thiosulphate, forms the basis of a good method for estimating $[\text{Cu}^{2+}]$ in a solution.

Q: An excess of potassium iodide solution was added to a 25 cm^3 sample of a solution of a copper(II) salt. The liberated iodine required 15 cm^3 of $0.010 \text{ mol dm}^{-3}$ sodium thiosulphate to discharge its colour. Calculate the $[\text{Cu}^{2+}]$ in the solution.

A similar effect takes place when cyanide ions are added to a copper(II) salt solution.



In this case the copper(I) cyanide will dissolve in an excess of the cyanide solution.



- (b) The $\text{Cu}^+(\text{aq})$ ion is removed by giving it access to a ligand with which it can form a very stable complex. For instance, copper(I) chloride may be brought into solution in concentrated hydrochloric acid, when the complex $[\text{CuCl}_2]^-$ is formed. This colourless, linear copper(I) complex is formed during the preparation of copper(I) chloride by the reduction with copper of a solution of copper(II) chloride in concentrated hydrochloric acid.

(e) complexes

The common geometries for Cu(II) complexes are octahedral and tetrahedral. Octahedral complexes are never symmetrical, however: as has been mentioned in Section A8(b), the blue hexa-aquo ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ contains two Cu-O bonds longer than the other four. The common tetra-ammine formed when ammonia solution is added to a solution of $\text{Cu}^{2+}(\text{aq})$ contains two water molecules still bonded to the copper, in the *trans* positions:

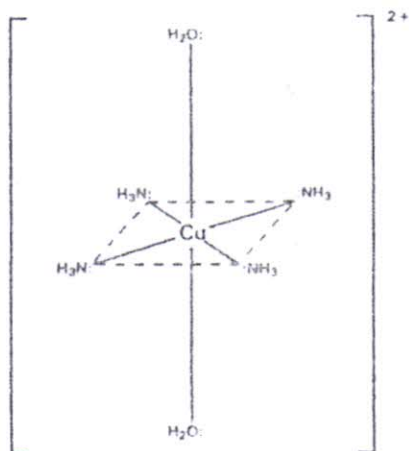


Fig B8.1

Some of the important precipitation and complex ion-forming reactions of the familiar $\text{Cu}^{2+}(\text{aq})$ are summarised below.

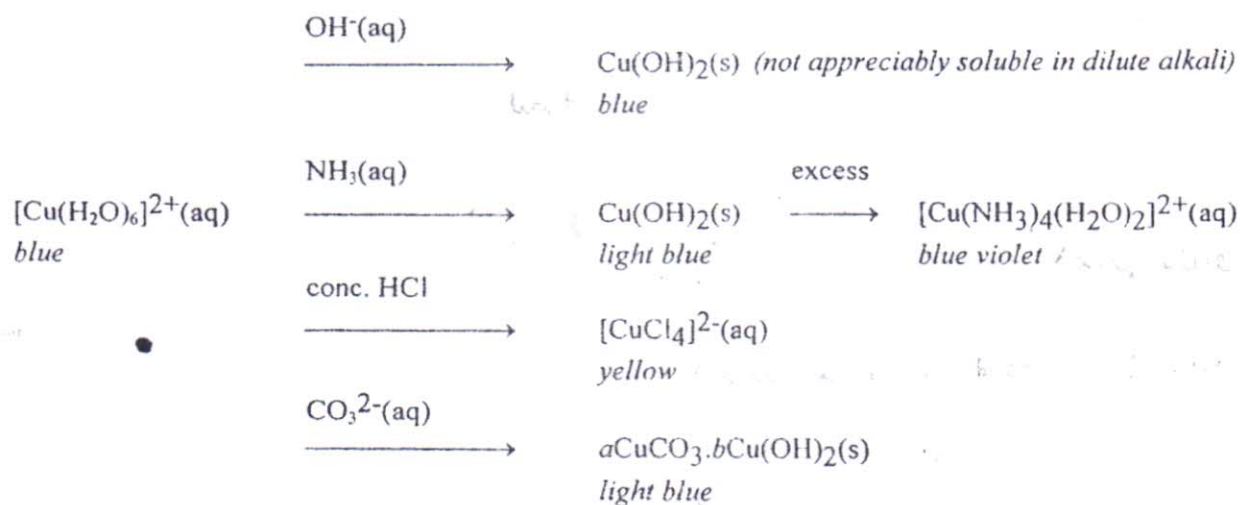
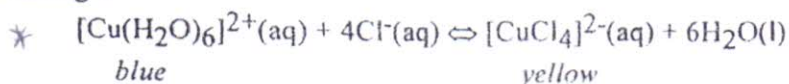


Fig B8.2

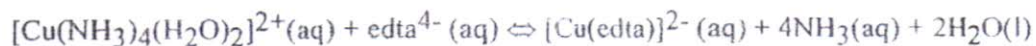
The chemistry of $\text{Cu}^{2+}(\text{aq})$ can often be interpreted in terms of stability constants.

complex	$[\text{CuCl}_4]^{2-}$	$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$	$[\text{Cu}(\text{edta})]^{2-}$
lg K	5.6	13.1	18.8

A blue solution of copper(II) sulphate turns green on the addition of concentrated hydrochloric acid as chloride ions gradually replace the water ligands in the blue ion $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}(\text{aq})$ to give the more stable yellow ion $[\text{CuCl}_4]^{2-}(\text{aq})$. The presence of both these ions in solution produces a green colour. Dilution of the solution reverses the colour change.

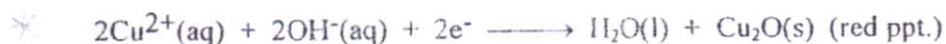


If a deep blue solution containing the $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ ion is treated with edta, the colour lightens considerably as the ammonia and water ligands are replaced by the hexadentate edta ligand to form the more stable and lighter coloured complex $[\text{Cu}(\text{edta})]^{2-}$.



(f) other compounds and reactions

Copper(II) sulphate is a component of various fungicides ("Bordeaux mixture") for grapes, and algicides for water purification. Cu(II) in alkaline conditions, stabilised in solution by complexing with anions of organic acids, is used in reagents such as Benedict's and Fehling's solutions, to test for the presence of mild reducing agents such as aldehydes. Reduction occurs to Cu(I) oxide:



(g) summary of the chemistry of copper

- main oxidation states are +1 and +2
- the +1 state is unstable to disproportionation in aqueous solutions
- stereochemistry of Cu(II) complexes is distorted octahedral or tetrahedral
- Cu(II) complexes are paramagnetic, whereas Cu(I) compounds are diamagnetic

Suggested Answers and Points Arising from Questions in Text

Section A

- §2 (b) Decrease mainly due to additional electrons going into the *same* shell (3d), thus experiencing little additional shielding, but experiencing an increasing pull from the increasing nuclear charge. Assuming for simplicity that atoms pack together as cubes,

$$\text{Density} = (\text{relative atomic mass}) \times (\text{mass of proton}) / 8r^3$$

$$\text{For Ti, density} = 47.9 \times 1.67 \times 10^{-24} / 8(0.147 \times 10^{-7})^3$$

$$= 3.14 \text{ g cm}^{-3}$$

likewise, for Mn, density = 4.43 g cm^{-3}

and Fe, density = 5.79 g cm^{-3}

In each case the calculated density is less, due to close packing being more efficient than simple cubic packing.

- §4 NO_2 (1 unpaired electron) \sim TiCl_3 (1 e^-) $<$ VCl_3 (2 e^-) $<$ MnCl_2 (5 e^-). NH_3 and TiO_2 have no unpaired electrons.



oxygen should oxidise iron(II) ions to iron(III), since +1.23 V is more positive than +0.77 V



(since H^+ ions are used up, the reaction will turn alkaline, and hydroxides can be precipitated.)

There will be no reaction between oxygen and acidified manganate(VII) ions, because both are the **oxidised** form of their respective couples.

- §7 Examples could be $\text{Mn}^{3+}/\text{Mn}^{2+}$ at +1.49 V and $\text{VO}_2^+/\text{VO}^{2+}$ at +1.00 V

- §8 (c) (iii) The isomer with no dipole moment has the two Cl ligands *trans* to each other, and the two bidentate diaminoethane ligands in a square-planar arrangement. The chiral isomers have the two Cl ligands *cis* to each other, with the two bidentate diaminoethane ligands arranged so that the planes of the 5-membered rings are at right angles. Two possible arrangements exist for such a geometry.

- §8 (c) (iv) Chlorine covalently bound to chromium will not react with Ag^+ , so adding $\text{AgNO}_3(\text{aq})$ will produce a ppt. of AgCl only with the ionised chlorine. If dried and weighed, the mass of the ppt should be three times as much for the first isomer as for the third isomer, etc.

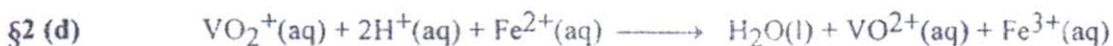
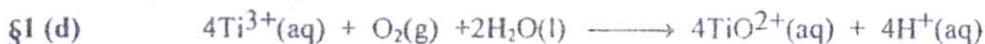
§8 (d) Combining the expressions for K_1 and K_2 in the text,

$$K_1 \times K_2 = \frac{[\text{Ag}(\text{H}_2\text{O})(\text{NH}_3)^+][\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{H}_2\text{O})_2^+][\text{Ag}(\text{H}_2\text{O})(\text{NH}_3)^+][\text{NH}_3]^2}$$

$$= \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{H}_2\text{O})_2^+][\text{NH}_3]^2}$$

which is the overall stability constant.

Section B



§2 (e) +2, +3, +4, +5, +3, +4, and +5.

§4 (d) $E^\circ_{\text{cell}} = 1.52 - 0.77 = 0.75 \text{ V}$



§5 (e) • $[\text{Fe}(\text{H}_2\text{O})\text{F}_5]^{2-}$ will form rather than $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$, since K_{stab} is larger.



$$E^\circ_{\text{cell}} = 1.81 - 1.23 = 0.58 \text{ V}$$



since $E^\circ (\text{Ni}(\text{OH})_3/\text{Ni}(\text{OH})_2) = 0.48 \text{ V}$, and overall $E^\circ_{\text{cell}} = 1.10 \text{ V}$,

therefore $E^\circ (\text{Cd}(\text{OH})_2/\text{Cd}) = 0.48 - 1.10 = -0.62 \text{ V}$

§8 (d) $[\text{Cu}^{2+}(\text{aq})] = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$

Further Questions from past A Level Papers

November 1991

- 3 (a) Describe with examples how two types of isomerism can occur in octahedral complexes of transition metals. [6]
- (b) Explain the following observations.
- (i) Passing air through an aqueous solution containing CoCl_2 , $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and HCl produces a green complex cation Y with formula:
- $$[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+ \quad [2]$$
- (ii) Evaporation of an aqueous solution of Y at 90°C produces a red complex cation Z, with the same formula as Y. Y has no dipole moment, whereas Z does. [2]

June 1992

- 2 (a) What is the origin of the colour of transition metal complexes? [4]
- (b) Explain the following colour changes:
- (i) addition of acidified aqueous tin(II) chloride to an aqueous solution containing a vanadium(IV) compound causes the colour to change from blue to green; [2]
- (ii) addition of concentrated hydrochloric acid to aqueous copper(II) sulphate causes the colour to change from blue to greenish-yellow; [2]
- (iii) cooling a warm solution of cobalt(II) chloride in dilute hydrochloric acid causes the colour to change from blue to pink. [2]

November 1992

- 1 (a) What features of transition metals allow them to show variable oxidation states? [2]
- (b) Both vanadium(III) and cobalt(III) ions are potentially unstable in water, but solutions of both survive for several hours.
- (i) Using suitable E^\ominus values from the *Data Booklet*, suggest likely products for the reactions of these two ions with water. [4]
- (ii) Suggest why it is possible to prepare aqueous solutions of these two ions, despite their potential instability. [1]
- (iii) Predict the products formed when each of these ions is separately added to a solution of vanadium(IV) sulphate, $(\text{VO})\text{SO}_4$. [3]

- 3 Iron(III) ions catalyse the reaction between iodide ions and peroxodisulphate ions ($\text{S}_2\text{O}_8^{2-}$) in aqueous solution.

- (a) What type of catalysis does this illustrate? [1]
- (b) By considering relevant E^\ominus values from the *Data Booklet* and below, describe and explain the role of iron(III) ions in this reaction.



Also on the basis of the E^\ominus values, choose **two** other examples of transition metal ions that would be predicted to act as catalysts for this reaction. What other factors might prevent the ions of your choice from behaving as catalysts? [7]

- (c) Transition metals are often used for industrial processes involving hydrogen. Give **two** examples of metals used in this way and describe the reactions they catalyse. [2]

June 1993

- 2 (a) By using different reagents, aqueous vanadium(V) ions can be reduced to lower oxidation states.

Use the *Data Booklet* to suggest the reagent you could use to obtain aqueous ions of

- (i) vanadium(II),
- (ii) vanadium(IV).

Write a balanced equation for each reaction.

Explain why the reagent you have chosen to produce vanadium(IV) ions does not further reduce the vanadium even when added in excess. [6]

- (b) A 0.0100 mol sample of an oxochloride of vanadium, VOCl_x , required 20.0 cm³ of 0.100 mol dm⁻³ acidified potassium manganate(VII) for oxidation of the vanadium.

By calculating

- (i) how many moles of electrons were removed by the MnO_4^- ions,
- (ii) the change in oxidation state of the vanadium,

deduce the value of x in the formula VOCl_x . [4]

November 1993

- 1 (a) Describe and explain what happens when dilute aqueous ammonia is gradually added to an aqueous solution containing $\text{Cu}^{2+}(\text{aq})$, followed by an aqueous solution of edta. [6]

- (b) Copper(I) sulphate is a white powder which reacts with water to give a blue solution and a pink-coloured solid.

(i) By reference to the relevant E^\ominus data from the *Data Booklet*, identify the two coloured products.

(ii) Describe the type of reaction undergone, and write a balanced equation. [4]

- 2 Because they are chemically similar, cobalt and iron are sometimes found together in ores.

Based on your knowledge of the properties and reactions of these elements and their compounds and using the *Data Booklet* where appropriate, describe

(a) in what ways these two elements have similar chemical properties, [1]

(b) how these chemical properties

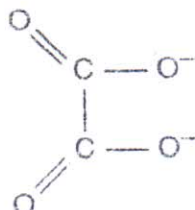
(i) are similar to,

(ii) differ from,

those of manganese and nickel.

June 1994

- 1 (a) (I) Explain what is meant by the *stoichiometry* of a transition metal complex.
- (II) Calculate the stoichiometry of the complex formed between iron and ethanedioate ions,



from the following data.

The potassium salt of the iron(III) ethanedioate complex has the following composition by mass:

K, 26.8%; Fe, 12.8%; C, 16.5%; O, 43.9% [4]

- (b) Suggest the geometry of the above complex and explain what type of isomerism it could show. [3]
- (c) When aqueous potassium thiocyanate, KSCN(aq), is added to a solution of the above complex, a red colour is observed. By contrast, when aqueous potassium thiocyanate is added to aqueous potassium hexacyanoferrate(III), no such red colour is formed.

Suggest an explanation for this difference. [3]

- 2 (a) Explain why transition elements often show variable oxidation states in their compounds, whereas other metals tend not to do so. [3]

- (b) Use the *Data Booklet* to predict the reactions, if any, that occur when **acidified** solutions containing the following pairs of reagents listed in (I) to (III) below are mixed.

Calculate the relevant overall E^\ominus values, and state the change in oxidation number of any transition metal during any reaction.

(I) MnO_4^- (aq) and Br^- (aq)

(II) Fe^{3+} (aq) and Cl_2 (aq)

(III) VO_2^+ (aq) and Sn^{2+} (aq) [7]

- 3 (a) Explain why aqueous ions containing transition metals are coloured, whereas aqueous ions of other metals are usually colourless. [You may wish to use $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ as examples.]
- (b) When an aqueous solution of the ligand L is mixed with an aqueous solution of chromium salt, the following equilibrium is set up:



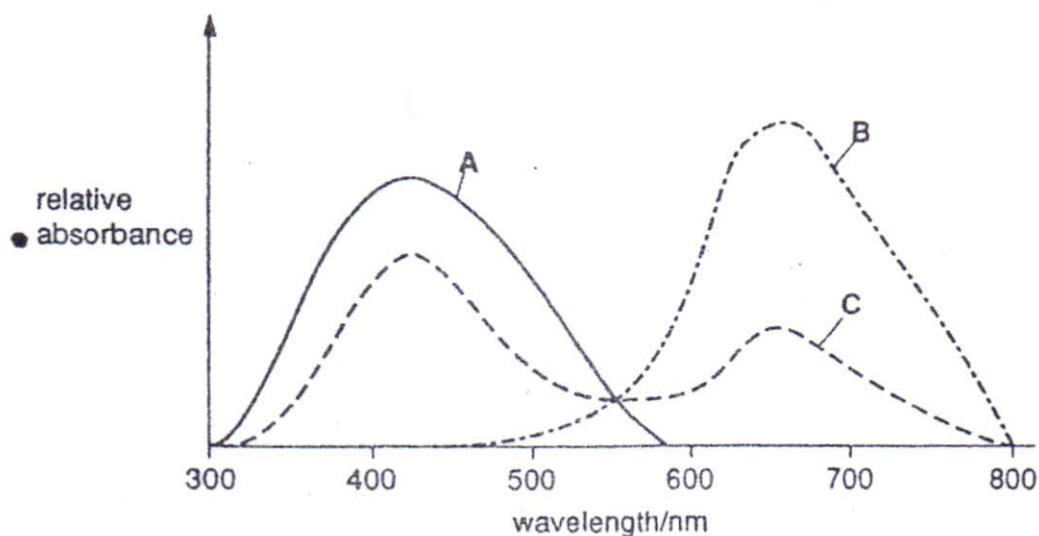
A similar equilibrium occurs with the ligand J , forming $[\text{Cr}J_6]^{3+}(\text{aq})$.

The equilibrium constants for these reactions are both large and similar to each other so that $[\text{Cr}^{3+}(\text{aq})]$ in the solution is very small in the presence of the ligands.

Solutions **A**, **B** and **C** were made up by mixing 0.1 mol dm^{-3} solutions of Cr^{3+} , L and J . The table below gives the volumes of each used.

solution	volumes of 0.1 mol dm^{-3} solution / cm^3		
	$\text{Cr}^{3+}(\text{aq})$	L	J
A	2	98	0
B	2	0	98
C	2	49	49

The visible absorption spectra of the three solutions **A**, **B** and **C** are shown below:

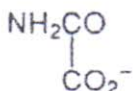


- (I) What are the colours of solutions **A** and **B**?
- (II) The spectra show that the peak in the curve for solution **B** is at a longer wavelength than is the peak in the curve for solution **A**.
What deduction can be made from this fact about the size of the d-orbital splitting in the two complexes?
- (III) The absorbance of a solution at a particular wavelength is proportional to the concentration of the ion responsible for the absorption.

Use this information and the given absorption spectra to suggest and explain whether ligand, L or J , forms the stronger bond with Cr^{3+} .

- 1 (a) (i) Describe the electrochemical processes that take place during the rusting of iron. Illustrate your answer with relevant half-equations.
- (ii) State **two** conditions that cause iron to rust more quickly. [6]
- (b) Use the above description to explain why the following objects rust slowly or not at all:
- (i) the hull of a ship to which small blocks of magnesium are bolted;
- (ii) a well-oiled bicycle chain. [4]

- 2 (a) Describe the bonding between the ligand and the ion of a transition metal in a complex. [2]
- (b) Explain the following observations.
- (i) Adding dilute aqueous ammonia to an aqueous solution containing Cu^{2+} ions causes the formation of a deep blue complex.
- (ii) Chromium forms a series of compounds with the general formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. One of these is violet and dissolves in water to form a solution from which all the chlorine can be precipitated as AgCl when aqueous silver nitrate is added. Another compound is green and produces an aqueous solution from which only one third of the chlorine can be precipitated with aqueous silver nitrate.
- (iii) The neutral complex formed between a Co^{2+} ion and two of the ions shown below,



is soluble in cyclohexane and in methylbenzene. [8]

- 3 (a) Explain the meaning of the terms *homogeneous catalysis* and *heterogeneous catalysis*. For each type, illustrate your answer by **one** specific reaction involving a transition metal (or transition metal compound). [5]
- (b) Aqueous hydrogen peroxide is fairly stable but, when a mixture of a cobalt(II) salt and tartaric acid, $\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$, is added to aqueous hydrogen peroxide, the following changes take place.

The initially pink solution slowly turns green and then oxygen is vigorously evolved. Finally, the solution turns pink again. Tartaric acid and the cobalt(II) salt can be recovered unchanged from the solution at the end.

- (i) Suggest
- 1 an explanation for the above observations;
 - 2 a role for the cobalt(II) salt and for the tartaric acid.
- Write an equation for the overall reaction. [5]

1 (a) Indicate the steps involved in the extraction of pure nickel from nickel(II) oxide by using its carbonyl complex, writing equations where appropriate and explaining why this particular method is used. [4]

(b) Aqueous solutions of nickel(II) salts are green due to the presence of the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (aq) ion. On adding aqueous ammonia to a solution of a nickel(II) salt, the colour changes to blue or purple as different complexes are formed through the displacement of H_2O ligands by N .

(i) Suggest a reason why NH_3 ligands displace H_2O ligands in the complex.

(ii) One of the intermediate complexes has the formula $\text{Ni}(\text{H}_2\text{O})_x(\text{NH}_3)_y\text{Cl}_2$.

Use the *Data* below to calculate:

(1) how many moles of complex are present in a 1.00 g sample;

(2) how many moles of ammonia are present in the 1.00 g sample;

(3) the formula of the complex.

Data

A 1.00 g sample of the complex produced 1.23 g of silver chloride when treated with an excess of aqueous silver nitrate.

A 1.00 g sample of the complex produced 0.29 g of ammonia when boiled with excess of aqueous sodium hydroxide.

(iii) What type of isomerism could this complex demonstrate?

2 (a) Describe the reactions, if any, that occur

(i) between I^- (aq) and Fe^{3+} (aq), both in the absence, and in the presence, of CN^- (aq)

(ii) when the precipitate formed between OH^- (aq) and Fe^{2+} (aq) is left exposed to

(b) By reference to the *Data Booklet*, explain the relative stabilities of the Fe(II)/Fe(III) oxidation states in the presence of

(i) OH^- (aq),

(ii) CN^- (aq).

(c) Use your answers to (b) to explain the reactions you have described in (a).