

UNIT 8: GROUP IV AND TRANSITION ELEMENTS

Recommended Prior Knowledge: The AS Units 1 and 2 should have been completed, along with the sections in A2 Sub-unit 6B dealing with E^\ominus values.

Context: These two sub-units can be studied on their own, or in conjunction with each other. Apart from the proviso above, they can be studied before or after the other A2 Units.

Outline: Sub-unit 8A covers the properties of the Group IV elements, from carbon to lead, and the properties and reactions of their oxides and chlorides. Sub-unit 8B covers the general physical properties of transition elements, some redox properties of iron, manganese and chromium compounds, some of the reactions of compounds of copper, and the origin of colour in transition element compounds

UNIT 8A: GROUP IV

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
9.3(a)	outline the variation in melting point and in electrical conductivity of the elements and interpret them in terms of structure and bonding	plotting graphs of the data is a useful exercise. Conductivity should be described only in terms of poor→semi→good (point out the difference between diamond and graphite), and explained in terms of localised or delocalised electrons (band theory as applied to Si and Ge is not required). The variation in melting point (high→medium→low) is best explained in terms of the interatomic bonding (strong macrocovalent, weaker covalent, metallic). A good illustration of the semi-conductive nature of a lump of silicon (if one is available) is the demonstration (using probes, battery and lamp) of the <i>increasing</i> conductivity on heating in a Bunsen flame (the lamp shining brighter).	M 96 C+H 18.1 R+N 11.1 site 8 (group II and group IV)
9.3(b)	describe and explain the bonding in, molecular shape and volatility of the tetrachlorides	All the tetrachlorides are tetrahedral, simple covalent structures. Their boiling points generally increase (CCl_4 is an exception) due to the increasing van der Waals attractions as a result of the larger number of electrons down the Group (although PbCl_4 is very unstable to heat, dissociating to $\text{PbCl}_2 + \text{Cl}_2$).	M 96 C+H 18.4 R+N 11.2
9.3(c)	describe and explain the reactions of the tetrachlorides with water in terms of structure and bonding	Carbon tetrachloride is very inert to water (and NaOH(aq)), even on heating. Explain the two reasons for this: the high strength of the C-Cl bond, and the absence of accessible d-orbitals on carbon that will allow the nucleophile (H_2O or OH^-) to bond to the central atom <i>before</i> the Cl^- leaves (the addition-elimination mechanism), thus lowering the activation energy. All other Group IV chlorides have accessible d-orbitals and ever-weakening M-Cl bonds, and so they increasingly readily hydrolyse in water from SiCl_4 to SnCl_4 .	M 96 C+H 18.4 R+N 11.3 site 3 (groups 3 and 4)
9.3(d)	describe and explain the bonding, acid-base nature and thermal stability of the oxides of oxidation states II and IV	Include revision of simple and giant molecular covalent (as in CO_2 , SiO_2 and GeO_2 - the dative bond in CO need not be covered) and ionic (as in SnO , PbO). SnO_2 and PbO_2 are most easily described as ionic, with the rutile structure, although some covalency occurs within the lattice. Acidity increases from the +II to the +IV oxidation state, and decreases from C to Pb. Thus CO is neutral whereas CO_2 acidic; PbO amphoteric whereas PbO_2 reacts more as an acidic than a basic oxide (e.g. it does not dissolve in aqueous acids, unless it oxidised them, but it does dissolve in concentrated NaOH(aq)). Enthalpy (and free energy) calculations show that CO should disproportionate to $\text{C} + \text{CO}_2$, whereas Pb should react with PbO_2 to form PbO . (Calculating these could be useful revision of unit 2 for students). PbO_2 evolves oxygen when heated (students can carry this out in the lab). Mention the stable mixed oxide Pb_3O_4 .	M 96 C+H 18.3 R+N 11.4 site 8 (group II and group IV) site 16 (periodicity)

9.3(e)	describe and explain the relative stability of higher and lower oxidation states of the elements in their oxides and aqueous cations, including - where relevant - E° values	Include examples of CO as a reducing agent (e.g. $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$) and PbO_2 as an oxidising agent (e.g. $\text{PbO}_2 + \text{HCl} \rightarrow \text{Cl}_2$). Point out that Sn^{2+} is a useful reducing agent, and give practice in predicting reactions using E° values for $\text{Sn}^{4+}/\text{Sn}^{2+}$ and $\text{Pb}^{4+}/\text{Pb}^{2+}$, and carrying them out in the test tube where possible. Suitable reagents to react with $\text{Sn}^{2+}(\text{aq})$ or $\text{Pb}^{4+}(\text{aq})/\text{PbO}_2$ include the follows: $\text{Br}^-(\text{aq})$, $\text{Br}_2(\text{aq})$, $\text{I}^-(\text{aq})$, $\text{I}_2(\text{aq})$, $\text{MnO}_4^-(\text{aq})$, $\text{Cr}_2\text{O}_7^{2-}(\text{aq})$.	M 96 C+H 18.3 R+N 11.5
9.3(f)	recognize the properties and uses of ceramics based on silicon(IV) oxide	briefly mention glass making, using $\text{Na}_2\text{CO}_3 + \text{SiO}_2$, and the higher melting properties of high-silica glass ("Pyrex") and quartz. Clays (and hence pottery and china) are based on aluminosilicate structures, which become cross-linked on baking, making them hard and high-melting.	M 96 C+H 18.3 R+N 11.6

UNIT 8B: TRANSITION ELEMENTS

AO	Learning Outcomes	Suggested Teaching Activities	Learning Resources
9.5(a)	explain what is meant by a <i>transition element</i> , in terms of d-block elements forming one or more stable ions with incomplete d orbitals	The definition should be learned. Although there are various other definitions in general use, note that this one excludes Sc and Zn, which have the electronic configuration $3d^0$ and $3d^{10}$ respectively in all their compounds.	M 105 C+H 19.2 R+N 13.1 site 4 (transition elements) site 8 (transition elements)
9.5(b)	state the electronic configuration of a first row transition element and of its ions	Student should practice writing out configurations in sub-shell notation (e.g. V is $1s^2 2s^2 2p^6 3s^2 3d^3 4s^2$, and Cr^{2+} is $1s^2 2s^2 2p^6 3s^2 3d^4$). The order of 3d and 4s as written down is irrelevant, but students should be aware that the 4s orbital is the first of the two to be filled, but also that the 4s electrons are the first to be lost. Cr and Cu have the $4s^1$ configuration in their neutral atoms.	M 105 C+H 19.2 R+N 13.2
9.5(c)	state that the atomic radii, ionic radii and first ionisation energies of the transition metals are relatively invariant	Explain that this is due to the extra 3d electrons entering an <i>inner</i> shell – thus to a large extent the increasing nuclear charge is shielded from the $4s^2$ electrons. There is no need at this level to describe or explain the detailed variation on these physical properties across the period – although the variations are there, they are comparatively small.	M 105 C+H 19.2 R+N 13.3
9.5(d)	contrast, qualitatively, the melting point; density; atomic radius; ionic radius; first ionisation energy and conductivity of the transition elements with those of calcium as a typical s-block element	Most of these properties can be explained by the extra protons in the nucleus of Fe, and by the extra electrons in the “valence” (i.e. 3d + 4s) shell. Thus melting point and conductivity are both higher because metallic bonding is greater (more delocalised electrons); density is greater because atomic mass is larger, but atomic radius is smaller. The first ionisation energies show the usual (slight) increase across a group.	M 105 C+H 19.2 R+N 13.4
9.5(e)	describe the tendency of transition elements to have variable oxidation states	Suitable examples could be Cr(III) and Cr(VI); Mn(II), Mn(IV) and Mn(VII); Fe(II) and Fe(III). These could be illustrated with laboratory samples. The demonstration of the reduction by zinc of a yellow solution of acidified V(V), through the blue V(IV) and the green V(III) to the violet V(II) never fails to impress students, especially if the final solution is mixed with the initial one in ratios of 1:2 and 2:1 (producing solutions containing V(IV) and V(III) respectively).	M 105 C+H 19.3 R+N 13.5
9.5(f)	predict from a given electronic configuration, the likely oxidation states of a transition element.	The most common oxidation state is +II, corresponding to the loss of the 4s electrons. This is always ionic (M^{2+}). The highest oxidation state corresponds to the “loss” of all the 3d + 4s electrons. This is often covalent (e.g. CrO_4^{2-} or MnO_4^-). All oxidation states in between these extremes are usually possible, although not necessarily stable.	M 105 C+H 19.3 R+N 13.6
9.5(g)	describe and explain the use of Fe^{3+}/Fe^{2+} , MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems (see also Section 6)	Students should be familiar with the half equations associated with these redox couples, and should be able to balance overall equations involving them. The use of $KMnO_4$ titrations to estimate amounts of iron or Fe^{2+} , and the uses of $KMnO_4$ and $K_2Cr_2O_7$ as oxidising agents in organic chemistry, should be covered.	M 107 C+H 19.3 R+N 13.16 site 7 (N-ch5-02, 03)
9.5(h)	predict, using E^\ominus values, the likelihood of redox reactions	Student should be given practice in the use of E^\ominus values for the above redox systems, and also for others involving transition elements (e.g. vanadium) to predict reactions with common oxidising	M 106 C+H 19.6

		and reducing agents (e.g. Cl_2 , I^- , SO_2 , Sn^{2+} etc)	
9.5(i)	explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) ions with water, hydroxide and ammonia	<p>A ligand should be defined as a molecule or ion with a lone pair of electrons, capable of forming a dative bond to a metal atom. A complex should likewise be defined as a molecule or ion containing a central metal ion surrounded by one or more ligands. The equilibria</p> $[\text{Cu}(\text{H}_2\text{O})_6]^{2+} + 2\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 2\text{NH}_4^+$ <p>and $[\text{Cu}(\text{H}_2\text{O})_4(\text{OH})_2](\text{s}) + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+} + 2\text{H}_2\text{O} + 2\text{OH}^-$</p> <p>and their associated colour changes, could be studied by adding $\text{NH}_3(\text{aq})$ gradually to $\text{Cu}^{2+}(\text{aq})$, and subsequent gradual acidification.</p> <p>Another system that's worth demonstrating is the classic red complex formed by $\text{Ni}^{2+}(\text{aq})$ and "dimethylglyoxime", $\text{CH}_3\text{C}(\text{=NOH})\text{-C}(\text{=NOH})\text{CH}_3$.</p>	<p>M 106 C+H 19.4 R+N 13.8 P(A2) 17 site 2 (Ni(II) complexes) site 10 (complexes) site 21a</p>
9.5(j)	explain qualitatively that ligand exchange may occur, including the complexes of copper(II) ions with water, hydroxide and ammonia	<p>Apart from the copper(II)-ammonia system described above, other systems to use for demonstration of ligand exchange could include:</p> <p>$\text{Cu}^{2+}(\text{aq}) + \text{conc HCl}(\text{aq}) \longrightarrow [\text{CuCl}_4]^{2-}$, followed by dilution;</p> <p>$\text{Fe}^{3+}(\text{aq}) + \text{SCN}^-(\text{aq})$, followed by $\text{F}^-(\text{aq})$ to discharge the colour by (displacing the SCN ligand with F).</p>	<p>M 106 C+H 19.4 R+N 13.10 P(A2) 18</p>
9.5(k)	describe the shape and symmetry of the d orbitals, and the splitting of degenerate d orbitals into two energy levels in octahedral complexes using the complexes of copper(II) ions with water and ammonia as examples	<p>Some time may need to be spent on this, since it's not only the shapes, but also the relative positions, of the d orbitals that are important. By placing the six ligands on the x, y and z axes, and directing the $d(z^2)$ and the $d(x^2-y^2)$ orbitals along those axes, students should be shown that electrons in those orbitals will be at a higher level than those in the other three d orbitals, that are pointing between the axes.</p> <p>Three-dimensional models of the orbitals would help in visualising this effect, if available.</p>	<p>M 105 C+H 19.5</p>
9.5(l)	explain the origin of colour in transition element complexes resulting from the absorption of light energy as an electron moves between two non-degenerate d orbitals	<p>There are two important things to stress here. One is that the colour is due to the <i>absorption</i> of light, as the electron uses the photon's energy to move from the lower energy level to the higher, and the other is that the colour observed is the <i>complement</i> of the colour absorbed. Thus $\text{Cu}^{2+}(\text{aq})$ ions absorb red and yellow light, so appear blue. Plotting absorption curves with a spectrometer would help student to see this – if one is available!</p>	<p>M 105 C+H 19.5 R+N 13.14</p>
9.5(m)	describe, in qualitative terms, the effects of different ligands on the absorption, and hence colour, using the complexes of copper(II) ions with water, hydroxide and ammonia as examples	<p>Students should be made aware that the more nucleophilic the ligand (i.e. more basic, as NH_3 is compared to H_2O), the larger the energy gap between the two sets of d orbitals is, and hence the higher is the frequency of absorption.</p>	<p>M 105 C+H 19.5 site 7 (N-ch5-08)</p>