

A2 Chemistry Module 5 – Specifications

Part 1 Thermodynamics

Enthalpy change (ΔH)

You should be able to define and apply the terms:

- enthalpy of formation,
- ionisation enthalpy,
- enthalpy of atomisation of an element and of a compound,
- bond dissociation enthalpy,
- electron affinity,
- lattice enthalpy (defined as either lattice dissociation or lattice formation),
- enthalpy of hydration and enthalpy of solution.

You should be able to:

- construct a Born–Haber cycle for the formation of simple ionic compounds.
- calculate enthalpies of solution for ionic compounds from lattice enthalpies and enthalpies of hydration.
- use mean bond enthalpies to calculate an approximate value of ΔH for other reactions.
- explain why values from mean bond enthalpy calculations differ from those determined from enthalpy cycles.

Free energy change ΔG and entropy change ΔS

You should be able to:

- understand that ΔH , whilst important, is not sufficient to explain spontaneous change (e.g. spontaneous endothermic reactions).
- understand that the concept of increasing disorder (entropy change ΔS) accounts for the above deficiency, illustrated by physical change (e.g. melting, evaporation) and chemical change (e.g. dissolution, evolution of CO_2 from hydrogencarbonates with acid).
- understand that the balance between entropy and enthalpy determines the feasibility of a reaction; know that this is given by the relationship $\Delta G = \Delta H - T\Delta S$ (derivation **not** required).
- be able to calculate entropy changes from absolute entropy values.

Part 2 Periodicity

Study of the reactions of Period 3 elements Na – Ar to illustrate periodic trends

You should be able to describe the trends in the reactions of:

- the elements Na and Mg with water.
- the elements Na, Mg, Al, Si, P and S with oxygen, limited to the formation of Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} and SO_2 .
- the elements Na, Mg, Al, Si and P with chlorine, limited to the formation of NaCl , MgCl_2 , AlCl_3 , SiCl_4 and PCl_5 .

A survey of the acid-base properties of the oxides of Period 3 elements

You should:

- understand the link between the physical properties of the highest oxides of the elements Na – S and their structure and bonding.
- be able to describe the reactions of the oxides of the elements Na – S with water, limited to Na_2O , MgO , Al_2O_3 , SiO_2 , P_4O_{10} , SO_2 and SO_3 .
- know the change in pH of the resulting solutions across the Period.
- be able to explain the trends in these properties in terms of the type of bonding present.
- be able to write equations for the reactions which occur between these oxides and given simple acids and bases.

A survey of the reactions of the chlorides of Period 3 elements with water

You should:

- understand the link between the physical properties of the chlorides of the elements Na – P and their structure and bonding.
- be able to describe the reactions of the chlorides of the elements Na – P with water, limited to NaCl , MgCl_2 , AlCl_3 , SiCl_4 and PCl_5 .
- know the change in pH of the resulting solutions across the Period.
- be able to explain the trends in these properties in terms of the type of bonding present.

Part 3 Redox Equilibria

Variable oxidation state

You should:

- understand oxidation and reduction as electron transfer reactions applied to reactions of d block elements.
- know and be able to apply the rules for assigning oxidation states in order to work out the oxidation state of an element in a compound from its formula.
- understand that changes in oxidation state involve redox processes.
- be able to write half-equations identifying the oxidation and reduction processes in redox reactions when the reactants and products are specified.
- be able to combine half-equations to give an overall redox equation.

Electrode potentials

You should:

- know the IUPAC convention for writing half-equations for electrode reactions.
- know and be able to use the conventional representation of cells.
- understand how cells are used to measure electrode potentials by reference to the standard hydrogen electrode and know that secondary standards are normally used.
- know the importance of the conditions when measuring the electrode potential, E (Nernst equation not required).
- know that standard electrode potential, E^\ominus , refers to conditions of 298 K, 100 kPa and 1 M solution of ions.

Electrochemical series

You should:

- know that standard electrode potentials can be listed as an electrochemical series.
- be able to use E values to predict the direction of simple redox reactions and to calculate the e.m.f of a cell.

Part 4 Transition metals

General properties of transition metals

You should know that:

- transition metal characteristics of elements Sc – Cu arise from an incomplete d sub-shell in atoms or ions.
- these characteristics include complex formation, formation of coloured ions, variable oxidation state and catalytic activity.

Complex formation

You should:

- be able to define the term ligand.
- know that co-ordinate bonding is involved in complex formation.
- understand that a complex is a central metal ion surrounded by ligands.
- know the meaning of co-ordination number.
- understand that ligands can be
 - unidentate (e.g. H_2O , NH_3 and Cl^-), or
 - bidentate (e.g. $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and $\text{C}_2\text{O}_4^{2-}$), or
 - multidentate (e.g. EDTA^{4-}).
- know that haem is an iron(II) complex with a multidentate ligand.

Shape of complex ions

You should know that:

- transition metal ions commonly form octahedral complexes with small ligands (e.g. H_2O and NH_3).
- transition metal ions commonly form tetrahedral complexes with larger ligands (e.g. Cl^-).
- Ag^+ commonly forms linear complexes, (e.g. $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ and $[\text{Ag}(\text{CN})_2]^-$).

Formation of coloured ions

You should know that:

- transition metal ions can be identified by their colour, limited to the complexes in this module.
- know that colour changes arise from changes in oxidation state, co-ordination number and ligand.
- know that colour arises from electronic transitions from the ground state to excited states: $\Delta E = h\nu$.
- know the use of ultraviolet and visible spectrophotometry in determining the concentration of metal ions in solution after the addition of a suitable ligand to intensify the colour.

Variable oxidation states

You should:

- know that transition elements show variable oxidation states.
- know that VO^{2+} , V^{3+} and V^{2+} are formed by reduction of VO_2^+ by zinc in acid solution.
- know that Cr^{3+} and Cr^{2+} are formed by reduction of $\text{Cr}_2\text{O}_7^{2-}$ by zinc in acid solution.
- know the redox titrations of Fe^{2+} with MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ in acid solution.
- be able to perform calculations for these titrations and for others when the reductant and its oxidation product are given.
- know the oxidation of Co^{2+} by air in ammoniacal solution.
- know the oxidations in alkaline solution of Co^{2+} and Cr^{3+} by H_2O_2 .

Catalysis

You should know that transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

Heterogeneous catalysis

You should:

- know that a heterogeneous catalyst is in a different phase from the reactants and that the reaction occurs at the surface.
- understand that adsorption of reactants at active sites on the surface may lead to catalytic action.
- know that the strength of adsorption helps to determine the activity (e.g. W too strong adsorption, Ag too weak adsorption, and so Ni and Pt are more useful).
- understand the use of a support medium to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).
- know that V_2O_5 is used as a catalyst in the Contact Process.
- know that Fe is used as a catalyst in the Haber Process.
- know that catalysts can become poisoned by impurities and consequently have reduced efficiency; and that this has a cost implication (e.g. poisoning by sulphur in the Haber Process and by lead in catalytic converters in cars).

Homogeneous catalysis

You should know that when catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species (e.g. the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ catalysed by Fe^{2+} , and autocatalysis by Mn^{2+} in titrations of $\text{C}_2\text{O}_4^{2-}$ with MnO_4^-).

Other applications of transition metal complexes

You should:

- understand the importance of variable oxidation states in catalysis; both heterogeneous and homogeneous catalysts, e.g. V_2O_5 in the Contact Process and autocatalysis by Mn^{2+} in MnO_4^- titrations.
- understand that Fe(II) in haemoglobin enables oxygen to be transported in the blood, and why CO is toxic.
- know that the Pt(II) complex cisplatin is used as an anticancer drug.
- understand that $[\text{Ag}(\text{NH}_3)_2]^+$ is in Tollen's reagent and $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ is formed in photography.
- know that $[\text{Ag}(\text{CN})_2]^-$ is used in electroplating.

Part 5 Reactions of Inorganic Compounds in Aqueous Solution

Lewis acids and bases

You should know the definitions of a Lewis acid and Lewis base; and understand the importance of lone pair electrons in co-ordinate bond formation.

Metal-aqua ions

You should know that metal–aqua ions are formed in aqueous solution:

$[\text{M}(\text{H}_2\text{O})_6]^{2+}$, limited to $\text{M} = \text{Fe}, \text{Co}$ and $\text{Cu} \dots$

$[\text{M}(\text{H}_2\text{O})_6]^{3+}$, limited to $\text{M} = \text{Al}, \text{V}, \text{Cr}$ and $\text{Fe} \dots$ and \dots

that these aqua ions can be present in the solid state (e.g. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$).

Acidity or hydrolysis reactions

You should understand the equilibria:

$[\text{M}(\text{H}_2\text{O})_6]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{M}(\text{H}_2\text{O})_5(\text{OH})]^+ + \text{H}_3\text{O}^+ \dots$ and \dots

$[\text{M}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{M}(\text{H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+ \dots$ to show generation of acidic solutions with M^{3+} , and very weakly acidic solutions with M^{2+} .

You should understand that the acidity of $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ is greater than that of $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ in terms of the polarising power (charge/size ratio) of the metal ion.

You should be able to describe and explain the simple test-tube reactions of:

- M^{2+} (aq) ions, limited to $\text{M} = \text{Fe}, \text{Co}$ and Cu , with the bases OH^- , NH_3 and CO_3^{2-} .
- M^{3+} (aq) ions, limited to $\text{M} = \text{Al}, \text{Cr}$ and Fe , with the bases OH^- , NH_3 and CO_3^{2-} .

You should know:

- that MCO_3 is formed but that $\text{M}_2(\text{CO}_3)_3$ is not formed.
- that some metal hydroxides show amphoteric character by dissolving in both acids and bases, e.g. hydroxides of Al^{3+} and Cr^{3+} .
- the equilibrium reaction $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$

Substitution reactions

You should:

- understand that the ligands NH_3 and H_2O are similar in size and are uncharged, and that ligand exchange occurs without change of co-ordination number, e.g. Co^{2+} and Cr^{3+} .
- know that substitution may be incomplete, e.g. the formation of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.
- understand that the Cl^- ligand is larger than these uncharged ligands, and that ligand exchange can involve a change of co-ordination number, e.g. Co^{2+} and Cu^{2+} .
- know that substitution with a bidentate or a multidentate ligand leads to a more stable complex.
- understand this chelate effect in terms of a positive entropy change in these reactions.