

3.5 A2 Unit F325: *Equilibria, Energetics and Elements*

This unit builds upon the chemical concepts that have been developed during AS Chemistry.

This unit consists of **three** teaching modules:

- Module 1: **Rates, Equilibrium and pH**
 - 5.1.1 How Fast?
 - 5.1.2 How Far?
 - 5.1.3 Acids, Bases and Buffers
- Module 2: **Energy**
 - 5.2.1 Lattice Enthalpy
 - 5.2.2 Enthalpy and Entropy
 - 5.2.3 Electrode Potentials and Fuel Cells
- Module 3: **Transition Elements**
 - 5.3.1 Transition Elements

Candidates are expected to apply knowledge, understanding and other skills gained in this unit to new situations and/or to solve related problems.

Recommended Prior Knowledge

Candidates should

- have studied AS Chemistry and, ideally, A2 unit F324.

5.1 Module 1: Rates, Equilibrium and pH

This module provides candidates with a quantitative study of physical chemistry. The material covered in this module links many areas of chemistry and explains many chemical phenomena. For example, the qualitative treatment of reaction rates and equilibria encountered at AS is developed within a quantitative and graphical context.

5.1.1 How Fast?

- orders, rate equations, rate constants;
- continuous and initial rate methods;
- rate-determining step.

5.1.2 How Far?

- equilibrium concentrations;
- the equilibrium constant, K_c .

5.1.3 Acids, Bases and Buffers

- acid–base equilibria;
- strength of acids including K_a ;
- pH determination, titration curves and buffer solutions.

Links

AS Unit F321: *Atoms, Bonds and Groups*

1.1.3 Acids;

1.3.2 Group 2 (acid reactions with metals, carbonates and bases).

AS Unit F322: *Chains, Energy and Resources*

2.3.2 Rates and Equilibrium.

5.1.1 How Fast?

Context and exemplification

Assessable learning outcomes

Rate graphs and orders

- Concentration–time can be plotted from continuous measurements taken during the course of a reaction (continuous monitoring).
- Initial rates require separate experiments using different concentrations of one of the reactants. Clock reactions are an approximation of this method.

Candidates should be able to:

- (a) explain and use the terms: *rate of reaction*, *order*, *rate constant*, *half-life*, *rate-determining step*;
- (b) deduce, from a concentration–time graph, the rate of a reaction and the half-life of a first-order reaction;
- (c) state that the half-life of a first-order reaction is independent of the concentration;
- (d) deduce, from a rate–concentration graph, the order (0, 1 or 2) with respect to a reactant;
- (e) determine, using the initial rates method, the order (0, 1 or 2) with respect to a reactant;

Rate equations; rate constants

- Integrated forms of rate equations are not required.

- (f) deduce, from orders, a rate equation of the form: $\text{rate} = k[\text{A}]^m[\text{B}]^n$, for which m and n are 0, 1 or 2;
- (g) calculate the rate constant, k , from a rate equation;
- (h) explain qualitatively the effect of temperature change on a rate constant and hence the rate of a reaction;

Rate-determining step

How Science Works 1, 7a:

- Use of rate equations to predict and propose a reaction mechanism.

- (i) for a multi-step reaction:
 - (i) propose a rate equation that is consistent with the rate-determining step,
- (ii) propose steps in a reaction mechanism from the rate equation and the balanced equation for the overall reaction.

5.1.2 How Far?

Context and exemplification

Assessable learning outcomes

Equilibrium

- Candidates will not be required to solve quadratic equations.

Candidates should be able to:

- (a) calculate, given appropriate data, the concentration or quantities present at equilibrium;
- (b) deduce, for homogeneous reactions, expressions for the equilibrium constant K_c ;
- (c) calculate the values of the equilibrium constant K_c including determination of units;
- (d) explain the effect of changing temperature on the value of K_c for exothermic and endothermic reactions;
- (e) state that the value of K_c is unaffected by changes in concentration or pressure or by the presence of a catalyst.

5.1.3 Acids, Bases and Buffers

Context and exemplification

Assessable learning outcomes

Brønsted–Lowry acids and bases

Candidates should be able to:

- (a) describe an acid as a species that can donate a proton and a base as a species that can accept a proton (see also unit F321: 1.1.3.a,h);
- (b) illustrate, using ionic equations, the role of H^+ in the reactions of acids with metals, carbonates, bases and alkalis (see also unit F321: 1.1.3.g; 1.1.4.f);
- (c) describe and use the term *conjugate acid–base pairs*;

Strong and weak acids

- (d) explain qualitatively, in terms of dissociation, the differences between *strong* and *weak* acids;
- (e) explain that the *acid dissociation constant*, K_a , shows the extent of acid dissociation;
- (f) deduce, for weak acids, expressions for K_a and pK_a ;

pH and $[H^+(aq)]$

- For a weak acid HA, assume:
 $[H^+(aq)] = [A^-(aq)]$;
equilibrium $[HA] = \text{undissociated } [HA]$.

- (g) define *pH* as $pH = -\log[H^+]$; $[H^+] = 10^{-pH}$;
- (h) state and use the expression for the *ionic product of water*, K_w ;

	<ul style="list-style-type: none"> (i) calculate pH from $[H^+(aq)]$ and $[H^+(aq)]$ from pH for: <ul style="list-style-type: none"> (i) strong monobasic acids, (ii) weak monobasic acids, (iii) strong bases, using K_w; (j) calculate K_a for a weak acid, given appropriate data;
Buffers: action, uses and calculations <ul style="list-style-type: none"> • The details of a basic buffer system are not required. • The H_2CO_3/HCO_3^- buffer is present in blood plasma, maintaining a pH between 7.35 and 7.45. 	<ul style="list-style-type: none"> (k) describe a <i>buffer solution</i> as a system that minimises pH changes on addition of small amounts of an acid or a base; (l) state that a buffer solution can be made from a weak acid and a salt of the weak acid, eg CH_3COOH/CH_3COONa; (m) explain the role of the conjugate acid–base pair in an acid buffer solution, eg CH_3COOH/CH_3COO^-, in the control of pH; (n) calculate the pH of a buffer solution, from the K_a value of a weak acid and the equilibrium concentrations of the conjugate acid–base pair; (o) explain the role of carbonic acid–hydrogencarbonate as a buffer in the control of blood pH;
Neutralisation	<ul style="list-style-type: none"> (p) for acid–base titration pH curves for strong and weak acids and bases: <ul style="list-style-type: none"> (i) interpret, or sketch, their shapes, (ii) explain the choice of suitable indicators for acid–base titrations, given the pH range of the indicator; (q) define and use the term <i>enthalpy change of neutralisation</i> and calculate enthalpy changes from appropriate experimental results (see also unit F322: 2.3.1.f.g).

Practical Skills are assessed using OCR set tasks. The practical work suggested below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Continuous monitoring of a reaction for ‘quantity’ against time graph:
 $CaCO_3/HCl$: monitoring gas or mass loss; $H^+/I_2/(CH_3)_2CO$: monitoring $[I_2]$ using a colorimeter.
- Clock reactions for determination of orders and rate constants by initial rates and rate concentration graphs:
 Iodine clocks: $I_2/S_2O_8^{2-}$ or $H^+/H_2O_2/I_2$ with $S_2O_3^{2-}$ (or vitamin C); Thiosulfate clock: $HCl/S_2O_3^{2-}$.
- The effect of temperature on reaction rates (clock reactions above are suitable).
- Determination of K_c for ethanoic acid/ethyl ethanoate equilibrium.
- Use of pH meters to: measure pHs of strong and weak acids; investigate buffer solutions.
- Generating an acid–base titration curve with a data logger, www.chemit.co.uk/uploads/java/.

5.2 Module 2: Energy

This module extends the study of energy encountered within unit F322: Chains, Energy and Resources. This module provides candidates with a deeper knowledge and understanding of chemical energy and also considers ways in which scientists are working to provide cleaner and more efficient energy.

The main areas of energy studied include:

5.2.1 Lattice Enthalpy

- lattice enthalpy and Born–Haber cycles.

5.2.2 Enthalpy and Entropy

- enthalpy *versus* entropy;
- free energy.

5.2.3 Electrode Potentials and Fuel Cells

- redox chemistry and electrochemical cells;
- fuel cells for the future.

Links

AS Unit F321: *Atoms, Bonds and Groups*

- 1.1.4 Redox.

AS Unit F322: *Chains, Energy and Resources*

- 2.3.1 Enthalpy Changes;
- 2.4.1 Chemistry of the Air.

5.2.1 Lattice Enthalpy

Context and exemplification

Assessable learning outcomes

Lattice enthalpy

Candidates should be able to:

- (a) explain and use the term *lattice enthalpy* (ΔH negative, ie gaseous ions to the solid lattice) as a measure of ionic bond strength;

Born–Haber and related enthalpy cycles

- (b) use the lattice enthalpy of a simple ionic solid (ie NaCl, MgCl₂) and relevant energy terms to:

Relevant Energy Terms:

enthalpy change of formation, ionisation energy, enthalpy change of atomisation and electron affinity.

- (i) construct Born–Haber cycles,
(ii) carry out related calculations;

How Science Works 1, 7a:

- Born–Haber cycle as a model for determination of lattice enthalpies and in testing the ionic model of bonding.

- (c) explain and use the terms *enthalpy change of solution* and *enthalpy change of hydration*;
- (d) use the enthalpy change of solution of a simple ionic solid (ie NaCl, MgCl₂) and

relevant energy terms (*enthalpy change of hydration*, and *lattice enthalpy*), to:

- (i) construct Born–Haber cycles,
 - (ii) carry out related calculations;
- (e) explain, in qualitative terms, the effect of ionic charge and ionic radius on the exothermic value of a lattice enthalpy and enthalpy change of hydration.

5.2.2 Enthalpy and Entropy

Context and exemplification

Assessable learning outcomes

Entropy

Candidates should be able to:

- (a) explain that entropy is a measure of the ‘disorder’ of a system, and that a system becomes energetically more stable when it becomes more disordered;
- (b) explain the difference in magnitude of entropy:
 - (i) of a solid and a gas,
 - (ii) when a solid lattice dissolves,
 - (iii) for a reaction in which there is a change in the number of gaseous molecules;
- (c) calculate the entropy change for a reaction given the entropies of the reactants and products;

Balance between entropy and enthalpy changes

- (d) explain that the tendency of a process to take place depends on temperature, T , the entropy change in the system, ΔS , and the enthalpy change, ΔH , with the surroundings;
- (e) explain that the balance between entropy and enthalpy changes is the *free energy change*, ΔG , which determines the feasibility of a reaction;
- (f) state and use the relationship $\Delta G = \Delta H - T\Delta S$;
- (g) explain, in terms of enthalpy and entropy, how endothermic reactions are able to take place spontaneously.

Context and exemplification

Assessable learning outcomes

Redox

Candidates should be able to:

- (a) explain, for simple redox reactions, the terms *redox*, *oxidation number*, *half-reaction*, *oxidising agent* and *reducing agent* (see also unit F321: 1.1.4);
- (b) construct redox equations using relevant half-equations or oxidation numbers;
- (c) interpret and make predictions for reactions involving electron transfer.

Electrode potentials

- E^\ominus data will be provided on examination papers.
- For E^\ominus measurements, ions of the same element can have concentrations of 1 mol dm^{-3} or be equimolar.

- (d) define the term *standard electrode (redox) potential*, E^\ominus ;
- (e) describe how to measure, using a hydrogen electrode, standard electrode potentials of:
 - (i) metals or non-metals in contact with their ions in aqueous solution,
 - (ii) ions of the same element in different oxidation states;
- (f) calculate a standard cell potential by combining two standard electrode potentials;

Feasibility of reactions

- (g) predict, using standard cell potentials, the feasibility of a reaction;
- (h) consider the limitations of predictions made using standard cell potentials, in terms of kinetics and concentration;

Storage and fuel cells

- Recall of a specific storage cell will not be required.
- Candidates will be expected to make predictions on supplied storage cells. All relevant electrode potentials and other data will be supplied.
- Hydrogen-rich fuels include methanol, natural gas, or petrol, which are converted into hydrogen gas by an onboard 'reformer'.

- (i) apply principles of electrode potentials to modern storage cells;
- (j) explain that a fuel cell uses the energy from the reaction of a fuel with oxygen to create a voltage;
- (k) explain the changes that take place at each electrode in a hydrogen–oxygen fuel cell;
- (l) outline that scientists in the car industry are developing fuel cell vehicles (FCVs), fuelled by:
 - (i) hydrogen gas,
 - (ii) hydrogen-rich fuels;
- (m) state advantages of FCVs over conventional petrol or diesel-powered vehicles, in terms of:
 - (i) less pollution and less CO_2 ,
 - (ii) greater efficiency;

How Science Works 6a:

- Development of fuel cells as an alternative to direct use of finite oil-based fuels in cars compared with logistical problems of their development and use.
- Pure hydrogen emits only water whilst hydrogen-rich fuels produce only small amounts of air pollutants and CO_2 .

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- Efficiency can be more than twice that of similarly sized conventional vehicles; other advanced technologies can further increase efficiency.
- How Science Works 7a, 7b:
- Political and social desire to move to a hydrogen economy has many obstacles including ignorance that energy is needed to produce hydrogen and that fuel cells have a finite life.
 - Hydrogen is an energy carrier and not a source.
- (n) understand how hydrogen might be stored in FCVs:
 - (i) as a liquid under pressure,
 - (ii) adsorbed on the surface of a solid material,
 - (iii) absorbed within a solid material;
 - (o) consider limitations of hydrogen fuel cells, for example:
 - (i) storing and transporting hydrogen, in terms of safety, feasibility of a pressurised liquid and a limited life cycle of a solid 'adsorber' or 'absorber',
 - (ii) limited lifetime (requiring regular replacement and disposal) and high production costs,
 - (iii) use of toxic chemicals in their production (see also unit F322: 2.4.2);
 - (p) comment that a 'hydrogen economy' may contribute largely to future energy needs but limitations include:
 - (i) public and political acceptance of hydrogen as a fuel,
 - (ii) handling and maintenance of hydrogen systems,
 - (iii) initial manufacture of hydrogen, requiring energy.
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Practical Skills are assessed using OCR set tasks. The practical work suggested below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Measuring enthalpy changes of solution.
 - Measuring an enthalpy change of neutralisation by a thermometric titration.
 - Redox reactions (test-tube scale):
 - metal displacements;
 - reactions involving colour changes.
 - Constructing electrochemical cells and measuring electrode potentials.
 - Making a fuel cell.
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5.3 Module 3: Transition Elements

This module extends the study of periodicity encountered within unit F321: Atoms, Bonds and Groups. By studying the transition elements, this module provides candidates with a deeper knowledge and understanding of inorganic chemistry and the Periodic Table. The module also links with many other areas of chemistry and provides many opportunities to consider chemistry synoptically.

5.3.1 Transition Elements

- general properties;
- precipitation reactions;
- ligands and complex ions;
- ligand substitution;
- redox reactions and titrations.

Links

AS Unit F321: *Atoms, Bonds and Groups*

- 1.1.4 Redox
- 1.3.2 Group 2

A2 Unit F325: *Equilibria, Energetics and Elements*

- 5.1.2 How Far?
- 5.2.3 Electrode Potentials and Fuel Cells

5.3.1 Transition Elements

Context and exemplification

Assessable learning outcomes

Properties

- Candidates should use sub-shell notation, eg for Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$.
- No detail of how colour arises is required.
- No detail of catalytic processes required.

Candidates should be able to:

- (a) deduce the electron configurations of atoms and ions of the d-block elements of Period 4 (Sc–Zn), given the atomic number and charge;
 - (b) describe the elements Ti–Cu as *transition elements*, ie d-block elements that have an ion with an incomplete d sub-shell;
 - (c) illustrate:
 - (i) the existence of more than one oxidation state for each element in its compounds,
 - (ii) the formation of coloured ions,
 - (iii) the catalytic behaviour of the elements and/or their compounds;
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<p>Precipitation reactions</p> <ul style="list-style-type: none"> • Non-complexed formulae such as $\text{Cu}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ are acceptable. • Oxidation of alkaline Fe(II) and Co(II) not required. 	<p>(d) describe, including ionic equations, the simple precipitation reactions and the accompanying colour changes of $\text{Cu}^{2+}(\text{aq})$, $\text{Co}^{2+}(\text{aq})$, $\text{Fe}^{2+}(\text{aq})$ and $\text{Fe}^{3+}(\text{aq})$ with aqueous sodium hydroxide;</p>
<p>Ligands and complex ions</p> <ul style="list-style-type: none"> • Examples should use H_2O, Cl^-, NH_3 as simple monodentate ligands. In examinations, other ligands might be introduced. 	<p>(e) explain the term <i>ligand</i> in terms of coordinate bonding;</p> <p>(f) state and use the terms <i>complex ion</i> and <i>coordination number</i>;</p> <p>(g) state and give examples of complexes with sixfold coordination with an octahedral shape;</p> <p>(h) explain and use the term <i>bidentate ligand</i> (eg $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, 'en');</p> <p>(i) describe the types of stereoisomerism shown by complexes, including those associated with bidentate and multidentate ligands:</p> <p style="padding-left: 40px;">(i) <i>cis-trans</i> isomerism, eg $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$,</p> <p style="padding-left: 40px;">(ii) optical isomerism, eg $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{2+}$;</p> <p>(j) describe the use of <i>cis-platin</i> as an anti-cancer drug and its action by binding to DNA in cancer cells, preventing division;</p>
<p>Ligand substitution</p>	<p>(k) describe the process of ligand substitution and the accompanying colour changes in the formation of:</p> <p style="padding-left: 40px;">(i) $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and $[\text{CuCl}_4]^{2-}$ from $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$,</p> <p style="padding-left: 40px;">(ii) $[\text{CoCl}_4]^{2-}$ from $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$;</p> <p>(l) explain the biochemical importance of iron in haemoglobin, including ligand substitution involving O_2 and CO;</p> <p>(m) state that the stability constant, K_{stab}, of a complex ion is the equilibrium constant for the formation of the complex ion in a solvent from its constituent ions;</p> <p>(n) deduce expressions for the stability constant, K_{stab}, of a ligand substitution, eg</p> $\text{M}^{2+}(\text{aq}) + 6\text{X}^-(\text{aq}) \rightleftharpoons \text{MX}_6^{4-}(\text{aq})$ $K_{\text{stab}} = \frac{[\text{MX}_6^{4-}(\text{aq})]}{[\text{M}^{2+}(\text{aq})][\text{X}^-(\text{aq})]^6}$ <p>(see also 5.1.2.b);</p> <p>(o) relate ligand substitution reactions of complexes to stability constants and understand that a large K_{stab} results in formation of a stable complex ion;</p>

Redox reactions and titrations

- Non-structured titration calculations could be examined in the context of both acid–base and redox titrations.
- (p) describe, using suitable examples, redox behaviour in transition elements;
- (q) carry out redox titrations, and carry out structured calculations, involving MnO_4^- and $\text{I}_2/\text{S}_2\text{O}_3^{2-}$;
- (r) perform non-structured titration calculations, based on experimental results.
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Practical Skills are assessed using specified OCR set tasks. The practical work outlined below may be carried out as part of skill development. Centres are not required to carry out all of these experiments:

- Precipitation of transition metal hydroxides (test-tube scale).
 - Ligand substitution reaction of complex ions (test-tube scale).
 - Redox titrations:
 - the estimation of iron in iron tablets titration with MnO_4^- in acid conditions;
 - the estimation of copper in alloys such as brass by titration using $\text{I}_2/\text{S}_2\text{O}_3^{2-}$.
-