

Are you ready for S315?



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1 Introduction

In S315 you will study important concepts in physical, inorganic, organic and biological chemistry and explore how these concepts shape our understanding of the natural and ‘synthetic’ world around us.

The module aims to develop your knowledge and understanding of:

- protein structure and function
- aqueous chemistry and its relationship to natural environments
- the roles that metals and their complexes play in living systems and in medicinal applications
- chemical reaction mechanisms, particularly in the context of atmospheric chemistry and catalysis
- how molecules can be designed
- the synthesis of organic molecules
- characterisation techniques to determine the structure of proteins, organic and inorganic molecules and surfaces

If you are intending to study S315, you will want to make sure that you have the necessary background knowledge and skills to be able to enjoy the module fully and to give yourself the best possible chance of completing it successfully.

Please read through these preparatory notes carefully, noting the assumed prior knowledge, and work through the self-assessment questions given in Sections 3, and 4. This is a useful exercise even if you have already completed the assumed prior courses for S315; working through these questions will serve as a reminder of some of the facts, skills and conceptual knowledge, which it is assumed you will bring with you from earlier modules. The answers are provided in Section 6. In Section 7 we have suggested sources of further reading that would help you to fill any gaps in your knowledge, or revise any areas of weakness.

If, after working through these notes, you are not sure about whether or not S315 is the right module for you, help and advice is available from the Study support team.

2 Assumed prior study

It is expected that you will have studied the Open University Level 2 chemistry module S215 *Chemistry: essential concepts* or its predecessor S205, *The Molecular World* (or equivalent study elsewhere), before study of S315, as well as the two Level 1 Science modules S104 and S141. Many of the chemical, mathematical and biological concepts in these level 1 and 2 modules are developed further in S315 – see Sections 3, 4 and 5 for the key concepts essential for S315.

If you are coming to S315 without having studied the assumed prior modules, then it is essential that you establish whether or not your background and experience give you a sound basis on which to tackle the work. If you find that you have difficulty in answering a significant number of the self-assessment questions, you are advised not to study S315 without first completing the study of the recommended prerequisite modules; please contact the Study support team for further advice.

3 Key concepts essential for S315

The key concepts listed below are covered in S215 (or S205) or S104 and S141 and a basic understanding of these is essential for S315. Although some of them are briefly described again and developed further in the S315 module materials, it is assumed that you are already familiar with these concepts. Self-assessment questions amplifying and illustrating a selection of this list of topics are included. You should be able to establish the level of understanding needed to study this module by working through them. You will find the answers to these questions in Section 6. You may find the S215 Summary and Data Book useful as you work through these questions. Some useful data which you may need to answer the question have been extracted from the S215 Summary and Data Book, and are presented in the Appendix in Section 8.

3.1 The Periodic Table

S315 draws on the following concepts and principles introduced in S215 Block 1 *The Periodic Table*.

- The electron configurations of the elements.
- Valence and core electrons.
- Electron spin.
- Atomic orbitals: s, p, d and f.
- The Periodic Table: the names of the elements and their symbols, the main-group elements (metals and non-metals) and the transition elements.
- Trends in bonding, covalent and ionic radii, electronegativity and ionisation energies.
- Covalent bonding by sharing electron pairs: single, double and triple bonds.
- Ionic bonding by electron transfer, cations and anions, simple ionic solids (e.g. NaCl).
- Lewis structures and resonance structures of molecules and ions.
- Coordinate (dative) bonding and coordination compounds.
- Ligands and simple metal complexes – monodentate, bidentate, tridentate, tetradentate and hexadentate ligands.
- The shapes of main-Group compounds – valence-shell electron-pair repulsion (VSEPR) theory.
- The properties of metals and of non-metals.
- Balancing chemical equations (stoichiometry).
- Molar quantities.
- Oxidation states and assignment of oxidation numbers.
- Oxidation–reduction (redox) equations.
- Acids and bases – definitions, pH, strong and weak, and their reactions.
- Polar and non-polar molecules.

It also is assumed that you are familiar with the following concepts from Book 7, Chapter 6 of S104.

- Radioactivity, half-life, chain-reaction, α - and β -radiation.

Question 3.1

This question refers to the Periodic Table.

- (a) What are the electron configurations of the elements with atomic numbers (i) 13, (ii) 22 and (iii) 36? In each case, indicate whether the element is a main-group element (state the Group) or a transition element.
- (b) In which Group of the Periodic Table do the atoms have the highest electronegativity in their Period?
- (c) In which Period do the atoms have the highest electronegativity in their Group?

Question 3.2

- (a) What type of bonding is present in:
 - (i) calcium fluoride (CaF_2);
 - (ii) diamond;
 - (iii) iron?
- (b) Draw Lewis structures and structural formulae for the following species and note if resonance structures are needed.
 - nitrogen trifluoride, NF_3 ;
 - sulfur hexafluoride, SF_6 ;
 - the sulfite ion, SO_3^{2-} .

Question 3.3

- (a) Calculate the oxidation numbers of the metal ions in the species:
 $\text{Cr}_2\text{O}_7^{2-}$, VO^{2+} , CrO_2^- and CrO_4^{2-} , and of Cl in OCl^- .
- (b) Write balanced equations for the reactions:
 - (i) between dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) and vanadium(III) (V^{3+}) ions in acidic aqueous solution, when VO^{2+} ions and chromium(III) ions are produced;
 - (ii) between sodium hypochlorite (NaOCl) and CrO_2^- ions in basic aqueous solution (OH^-), when CrO_4^{2-} and chloride ions are produced.
- (c) Describe the redox changes involved for the reactions in part (b).

Question 3.4

Potassium permanganate in acid solution oxidises thallium(I) to thallium(III) if excess fluoride ions are present. 20.00 cm^3 of a solution of 0.025 molar (mol dm^{-3}) KMnO_4 reacts with 10 cm^3 of 0.1 molar thallium(I) solution.

Calculate the number of moles of thallium(I) that react with one mole of permanganate, and hence the oxidation number of the manganese in the product.

Write a balanced equation for the reaction (in the products, the manganese is a six-coordinate fluoride complex and the oxygen appears in water).

Question 3.5

Acids and bases can be defined in different ways. Give the definition for an acid and a base according to the following theories: Arrhenius, Brønsted–Lowry, Lewis.

3.2 Chemical bonding

S315 draws on the following concepts and principles introduced in S215 Block 2, *Chemical bonding*.

- Atomic orbitals: representation.
- Molecular orbitals: bonding, non-bonding and antibonding, σ and π .
- The relationship between the overlap of atomic orbitals and the separation of the bonding and antibonding orbitals.
- Molecular-orbital energy-level diagrams of diatomic molecules and ions.
- Use of orbital energy-level diagrams in prediction of properties: stability, bond order, paramagnetism.
- Centre of symmetry: recognition, effect on labelling of molecular orbitals.

Question 3.6

Figure 1 shows a fully labelled molecular-orbital energy level diagram for the dinitrogen (N_2) molecule. Explain the origin of the molecular orbitals, and calculate the bond order of the molecule. Is the molecule paramagnetic or diamagnetic?

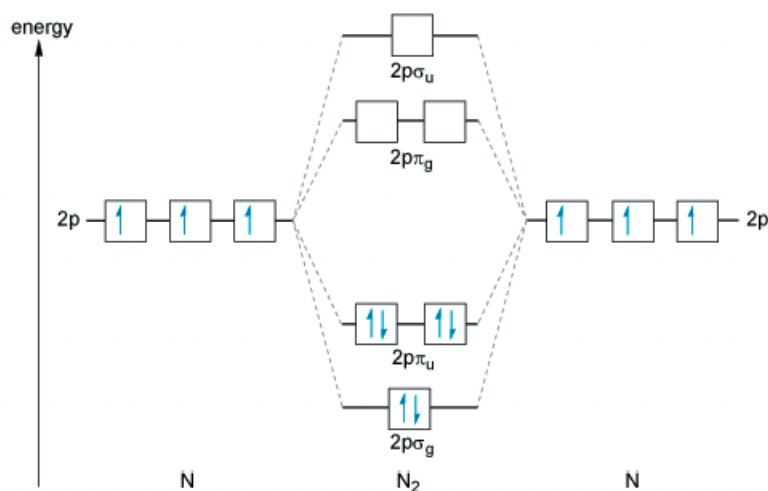


Figure 1 Molecular orbital energy level diagram for dinitrogen.

3.3 Organic molecules

S315 draws on the following concepts and principles introduced in S215 Block 3 *Organic molecules*. It is assumed that you will be able to use a chemical drawing package (Accelrys Draw or ACD ChemSketch) to produce representations of the structures of organic molecules.

- Structural formulae and the nomenclature of simple organic molecules: alkanes, homologues and isomers; saturated and unsaturated compounds;

functional groups: alkene, alkyne, halide, alcohol, ether, amine, aldehyde, ketone, acid, ester, amide, nitrile; aliphatic and aromatic compounds.

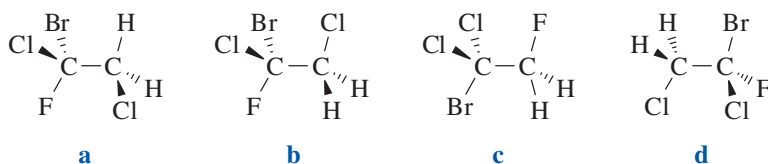
- Hybrid atomic orbitals from carbon (sp^3 , sp^2 , sp), correlation with structures and shapes of methane, ethane, ethene, ethyne, benzene.
- Stereochemistry: relative and absolute configurations.
- Newman and 'flying-wedge' projections.
- Geometric isomers: *cis/trans*, *Z/E*.
- Chirality, enantiomers, racemate: *R/S*, *meso*.
- The Cahn–Ingold–Prelog priority rules to specify the *R* or *S* configuration of chiral carbon atoms.
- Diastereoisomers.

Question 3.7

Select from the structures **a–d** molecules that are:

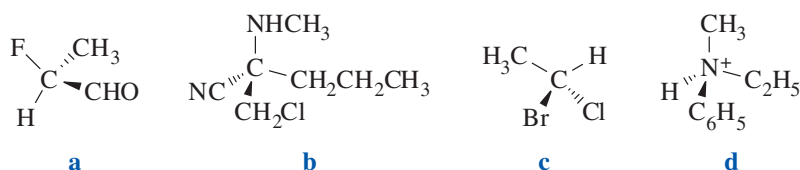
- stereoisomers;
- molecules with the same configuration at the chiral carbon atom;
- different conformations of the same molecule.

You may find it helpful to make models or draw Newman projections.



Question 3.8

Use the Cahn–Ingold–Prelog rules to specify the configuration of the following molecules:



Question 3.9

Draw a flying-wedge representation of the *meso* form of $(\text{CH}_3)\text{CICH}-\text{CHCl}(\text{CH}_3)$.

Question 3.10

Draw the possible isomers of the following compounds (a)–(e), labelling them as *E* or *Z* (and *cis* or *trans* if appropriate):

- $\text{ClHC}=\text{CHCl}$;

- (b) $\text{Cl}(\text{CH}_3)\text{C}=\text{CH}_2$;
- (c) $(\text{CH}_3)_2\text{C}=\text{CBrCl}$;
- (d) $(\text{C}_6\text{H}_5)\text{HC}=\text{CHCH}_3$;
- (e) $(\text{C}_6\text{H}_5)\text{ClC}=\text{CBrCH}_3$.

3.4 Chemical thermodynamics and equilibrium

S315 draws on the thermodynamic ideas introduced in S215 Block 4 *Thermodynamics and equilibrium*. In particular, you should be clear about the meaning of quantities such as $\Delta_{\text{m}}H^{\ominus}$, $\Delta_{\text{m}}S^{\ominus}$ and $\Delta_{\text{m}}G^{\ominus}$, and confident about calculating their values (for a given reaction) from tabulated thermodynamic data.

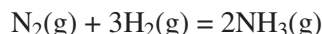
- The first law of thermodynamics: $\Delta H = q + w_{\text{el}}$.
- The second law of thermodynamics: for a natural (a spontaneous) process in an isolated system, $\Delta S_{\text{total}} > 0$.
- Thermicity: exothermic and endothermic reactions.
- The definition of ΔG (the Gibbs function or free energy change):
 $\Delta G = \Delta H - T\Delta S$.
- The criterion $\Delta G < 0$ for a spontaneous reaction at constant temperature and pressure.
- Tabulated thermodynamic data: standard enthalpies of formation ($\Delta_{\text{f}}H^{\ominus}$), standard Gibbs functions of formation ($\Delta_{\text{f}}G^{\ominus}$) and absolute entropies (S^{\ominus}).
- The standard molar enthalpy change for a reaction ($\Delta_{\text{m}}H^{\ominus}$):
 $\Delta_{\text{m}}H^{\ominus} = \sum \Delta_{\text{f}}H^{\ominus}(\text{products}) - \sum \Delta_{\text{f}}H^{\ominus}(\text{reactants})$
- The standard molar entropy change for a reaction ($\Delta_{\text{m}}S^{\ominus}$):
 $\Delta_{\text{m}}S^{\ominus} = \sum S^{\ominus}(\text{product}) - \sum S^{\ominus}(\text{reactant})$
- The standard molar free energy change for a reaction ($\Delta_{\text{m}}G^{\ominus}$):
either $\Delta_{\text{m}}G^{\ominus} = \sum \Delta_{\text{f}}G^{\ominus}(\text{product}) - \sum \Delta_{\text{f}}G^{\ominus}(\text{reactant})$
or $\Delta_{\text{m}}G^{\ominus} = \Delta_{\text{m}}H^{\ominus} - T\Delta_{\text{m}}S^{\ominus}$
- Chemical equilibrium and the equilibrium constant, K and reaction quotient, Q .
- Activity.
- The relationship of the standard molar free energy change to the equilibrium constant:
 $\Delta_{\text{m}}G^{\ominus} = -2.303 RT \log K$ (or $\Delta_{\text{m}}G^{\ominus} = -RT \ln K$)
- The relationship of the standard molar free energy change ($\Delta_{\text{m}}G^{\ominus}$) to the standard redox potential E^{\ominus} :
 $\Delta_{\text{m}}G^{\ominus} = -nFE^{\ominus}$, where $F = 96\,485 \text{ C mol}^{-1}$
- The Nernst equation: determination of the emf, E , under non-standard conditions:

$$E = E^{\ominus} - \frac{RT}{nF} \ln Q$$

Question 3.11

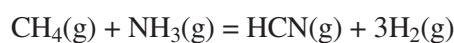
This question is concerned with the information in Table 1.

(a) The synthesis of ammonia is the basis of the Haber–Bosch process:



- (i) Calculate the value of $\Delta_{\text{m}}H^{\ominus}$ at 298.15 K. Is the reaction exothermic or endothermic?
- (ii) Calculate the value of $\Delta_{\text{m}}G^{\ominus}$ at 298.15 K. Is the reaction thermodynamically favourable at this temperature?
- (iii) Write down an expression for the equilibrium constant, K , for this reaction. If concentrations are expressed in mol dm^{-3} , what are the units of K ?

(b) Use information from Table 1 to decide whether the following reaction is thermodynamically favourable at 200 °C (473.15 K):



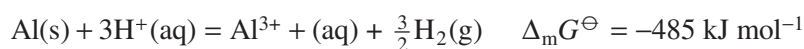
State any assumptions that you make.

Table 1 Thermodynamic data at 298.15 K for some pure substances.

Substance	State	$\frac{\Delta_{\text{f}}H^{\ominus}}{\text{kJ mol}^{-1}}$	$\frac{\Delta_{\text{f}}G^{\ominus}}{\text{kJ mol}^{-1}}$	$\frac{S^{\ominus}}{\text{J K}^{-1} \text{ mol}^{-1}}$
CH ₄	g	-74.8	-50.7	186.3
H ₂	g	0	0	130.7
N ₂	g	0	0	191.6
NH ₃	g	-46.0		192.5
HCN	g	135.1	124.7	201.8

Question 3.12

For the reaction of aluminium metal with an acid,



- (a) Give this equation in the usual form for a standard redox potential and calculate the value of $E^{\ominus}(\text{Al}^{3+}|\text{Al})$.
- (b) Does the value you have obtained suggest that aluminium is a powerful or weak oxidising or reducing agent?

3.5 Chemical kinetics

S315 draws on the following concepts and principles introduced in S215 Block 5 *Chemical kinetics*. Familiarity with the Graph Plotter from S215 is assumed.

- Schematic energy profiles: exothermic and endothermic.
- Activation energy.
- First and second order reactions.

- Propose a plausible rate equation.
- Reaction half-life: preliminary check for first-order reaction.
- Use of experimental data to determine rates of change, rate constants and partial orders of reaction.
- Isolation method and pseudo-order rate constants.
- Differentiation and integration methods.
- Use of appropriate software program that allows experimental data to be input, plotted and analysed (familiarity with the Graph Plotter from S215 is assumed).
- Arrhenius equation: effect of temperature on reaction rate.
- Composite and elementary reactions, molecularity.
- Rate-limiting step and pre-equilibrium.

Question 3.13

The reaction of $(\text{CH}_3)_2\text{CHBr}$ with potassium hydroxide was studied. Table 2 gives the concentration of $(\text{CH}_3)_2\text{CHBr}$ as a function of time. Potassium hydroxide was present in excess.

Table 2 Data from an experiment involving Reaction 1 for particular initial concentrations of the reactants.

time/s	$[(\text{CH}_3)_2\text{CHBr}]/10^{-3} \text{ mol dm}^{-3}$
0	150.3
30	125.3
60	102.8
90	85.0
120	74.8
150	61.6
210	42.8
270	28.6
330	20.5
390	13.9
450	10.3
510	7.3
600	4.4
900	1.5

Plot a reaction profile for this reaction. Use this to determine whether the reaction is first order with respect to $[(\text{CH}_3)_2\text{CHBr}]$.

Question 3.14

The rate constants for the gas phase decomposition of chloroethane to ethene and hydrogen chloride are shown in Table 3 for a range of different temperatures.

Table 3 Data from an experiment involving the gas phase decomposition of chloroethane at different temperatures.

T/K	k_R/s^{-1}
1100	2.45×10^2
1150	7.69×10^2
1200	2.19×10^3
1250	5.74×10^3
1300	1.40×10^4
1350	3.18×10^4
1400	6.84×10^4

Plot an appropriate graph based on these data to obtain the activation energy, E_a , of this reaction.

$$R = 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$$

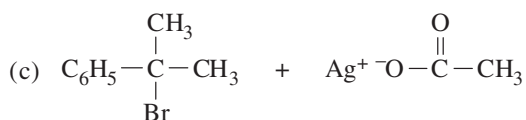
3.6 Organic reaction mechanisms

S315 draws on the following concepts and principles introduced in S215 Block 6 *An introduction to organic reaction mechanisms*.

- Classification of reactions: substitution, addition, elimination.
- Kinetic data to determine whether a reaction is unimolecular or bimolecular.
- Reaction-coordinate diagram; transition state; intermediate, energy profile.
- Use of ‘curly arrows’ to describe bond making and breaking.
- ‘Good’ and ‘poor’ nucleophiles, electrophiles, leaving groups.
- Basic S_N1/S_N2 , E1/E2 mechanisms of alkyl halides, etc.

Question 3.15

For each of the following reactions predict whether an S_N1 or S_N2 mechanism (or both) will be followed. Give your reasoning.

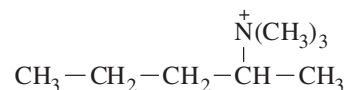


Question 3.16

Give the mechanism and products for the reaction of structure **1**:

(a) with sodium ethoxide ($CH_3CH_2O^- + Na$) via an E2 mechanism;

(b) with water via an E1 mechanism.



1

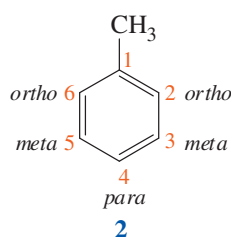
3.7 Alkenes and aromatic compounds

S315 draws on the following concepts and principles introduced in S215 Block 7 *Alkenes and aromatic compounds*.

- π -bonds in alkenes and alkynes.
- Conjugation of π systems and resonance.
- Electrophilic addition reactions: stability of carbocation intermediate.
- Addition to alkenes; 'Markovnikoff's rule'.
- Cyclic conjugation and resonance energy stabilization of benzene and derivatives.
- Electrophilic substitution reactions with retention of aromatic ring: nitration, bromination, Friedel–Crafts alkylation and acylation.
- *Ortho/para* versus *meta* directing groups: inductive and resonance effects.
- Synthetic uses of diazonium salts – substitution and coupling.

Question 3.17

Draw the resonance forms of the intermediate carbocation formed in the following reactions of an electrophile (X^+) with methylbenzene (toluene, **2**):



- reaction at a position *ortho* to the CH₃ group of methylbenzene (that is, positions 2 or 6 on the ring);
- reaction at a *meta* position (positions 3 or 5);
- reaction at the *para* position (position 4).
- On the basis of these resonance forms, predict the major product(s) from the mono-substitution of toluene (**2**) with chlorine, using AlCl₃/Cl₂.

3.8 Materials chemistry

S315 draws on the following concepts and principles introduced in S215 Block 8, *Materials chemistry*.

- Close-packing of spheres (cubic close-packing and hexagonal close-packing).
- Octahedral and tetrahedral holes in close-packed lattices.
- The body-centred cubic lattice and the structures of metals.
- Unit cells.
- Ionic solids – the sodium chloride, caesium chloride, fluorite and corundum lattices.
- Ionic radius.
- Defects in crystals – extrinsic and intrinsic, Schottky and Frenkel.

Question 3.18

- (a) Draw the unit cell for (i) a body-centred cubic lattice, and (ii) a face-centred cubic lattice of a metal.
- (b) Calculate the number of atoms in the body-centred and face-centred unit cells.

3.9 Molecular characterisation and spectroscopic analysis

S315 draws on the following concepts and principles introduced in S215 Block 9 *Molecular characterisation and spectroscopic analysis*.

- The electromagnetic spectrum: types of excitation possible in each region.
- Wavelength (λ), frequency (ν) and wavenumber (σ).
- The relationships $E = h\nu$ (where E is the energy of a photon), $\nu\lambda = c$ (speed of light, $c = 3 \times 10^8 \text{ ms}^{-1}$), and $\sigma = 1/\lambda$.
- UV–visible spectrum: conjugated and non-conjugated molecules.
- Beer–Lambert law.
- Vibrational spectroscopy: normal modes of vibration, infrared active, Raman active, group frequency charts.
- Dependency of vibrational frequency with atomic mass and bond strength.
- Strategy for interpreting IR spectra.
- ^{13}C nuclear magnetic resonance spectroscopy: magnetic equivalence, chemical shift, correlation charts, peak multiplicity, decoupled spectrum, off-resonance spectrum, DEPT.
- Strategy for interpreting ^{13}C NMR spectra.
- Mass spectrometry: molecular mass, molecular formula.
- Structure determination using combined techniques.

Question 3.19

Two of the absorptions in spectra of the molecule OCS are at $1.216 \times 10^{10} \text{ Hz}$ and $2.580 \times 10^{13} \text{ Hz}$.

- (a) What wavelengths and wavenumbers correspond to these frequencies?
- (b) In what regions of the electromagnetic spectrum do these frequencies lie?
- (c) What type of molecular energy change is likely to be responsible for each of these absorptions?

Question 3.20

Which of the following molecules will have a vibration that is active in (a) the infrared spectrum, (b) the Raman spectrum?

N_2 , HF, HCl, Br_2 and NO

Question 3.21

The ^{13}C NMR and infrared spectra of a compound with molecular formula $\text{C}_6\text{H}_{14}\text{O}$ are shown in Figures 2 and 3, respectively. The labels d, t and q on the spectrum refer to doublets, triplets and quartets produced by coupling to the hydrogen atoms attached to each particular carbon atom.

Use correlation charts to suggest two possible structures for the compound. Discuss in detail your interpretation of the spectra.

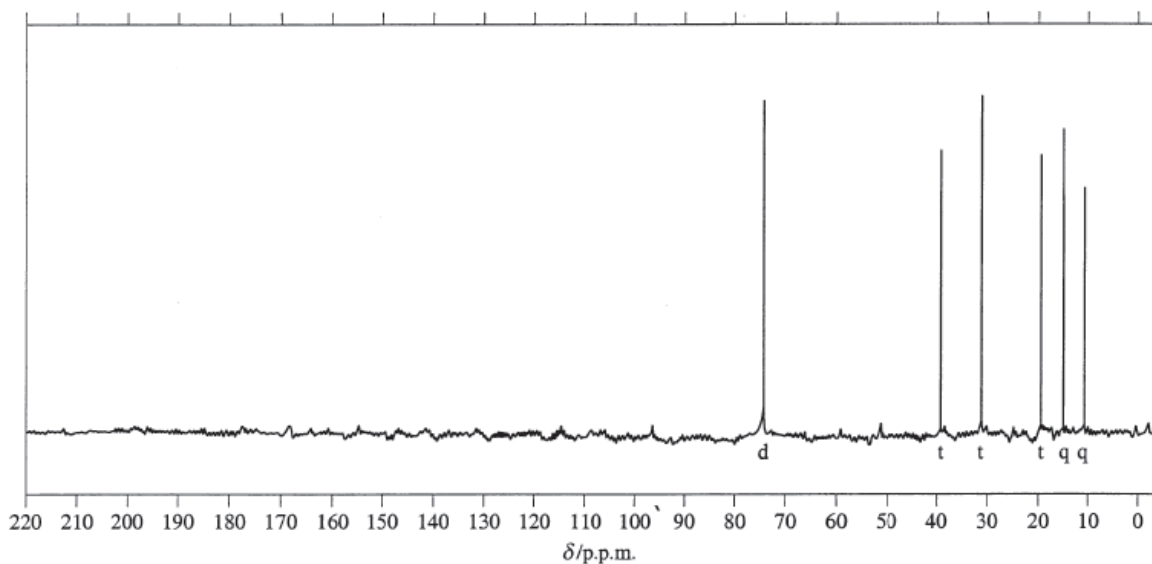


Figure 2 The ^{13}C NMR spectrum of an unknown compound (d, t and q indicate off-resonance C–H coupling patterns).

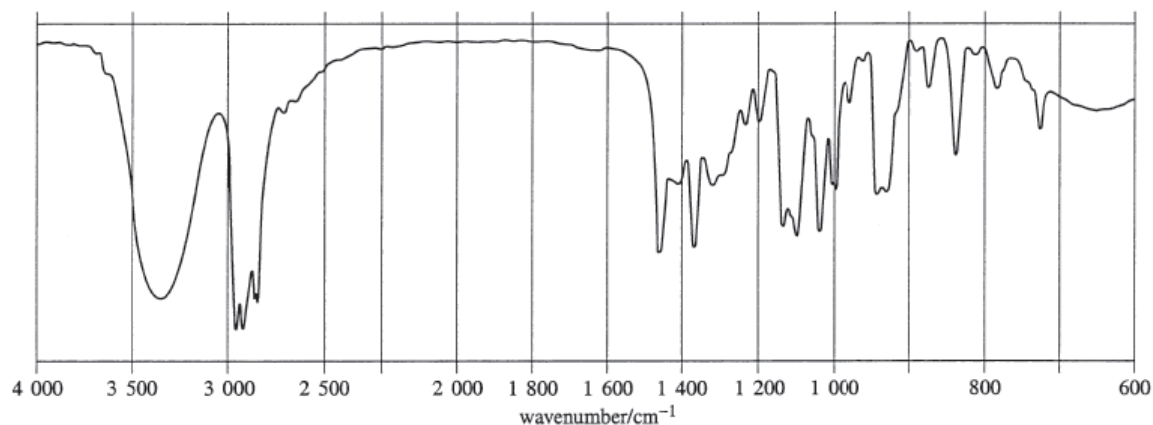


Figure 3 The infrared spectrum of an unknown compound.

3.10 Transition metal chemistry

S315 draws on the following concepts and principles introduced in S215 Block 10, *Introduction to the first-row transition elements*.

- Determination of d-electron configuration of atoms and ions.
- Transition-metal complexes: inner and outer sphere coordination, isomerism.
- Thermodynamic stability of metal complexes: chelate effect, hard and soft acids, Irving–Williams series.

- Nernst equation: relative stability of oxidation states with pH and ligand.
- Crystal-field theory: splitting of d orbital energy levels for octahedral and tetrahedral complexes, high- or low-spin, crystal-field stabilisation energy (CFSE), spectrochemical series.
- d–d absorption spectra: selection rules.
- Magnetic properties of transition-metal complexes.

Question 3.22

Draw the structural formulae (indicating any isomers) of:

- The tetrachloro zinc(II) complex ion $[\text{ZnCl}_4]^{2-}$;
- The bis-ethylenediamine nickel(II) complex $[\text{Ni}(\text{ethylenediamine})_2\text{Cl}_2]$; ethylenediamine is $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$.

Question 3.23

State the oxidation state of the metal ion and calculate the d-electron configuration for the following complex ions:

- $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- $[\text{CoCl}_4]^{2-}$
- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

Question 3.24

- Sketch a fully labelled energy-level diagram showing the 3d levels only for a transition-metal ion in an octahedral crystal field. In constructing your diagram start with the free ion and show the hypothetical situation if the ion were in a sphere of negative charge.
- Fill in the electrons for a d^5 transition metal ion in (i) a weak and (ii) a strong octahedral crystal field.

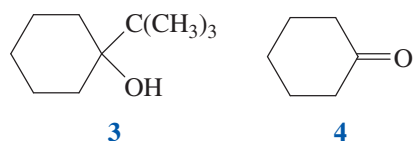
3.11 Carbonyl and organometallic chemistry

S315 draws on the following concepts and principles introduced in S215 Block 11 *Carbonyl and organometallic chemistry*.

- Nucleophilic addition to aldehydes and ketones by, e.g. hydride and Grignard reagents; tetrahedral intermediate; addition-elimination reactions with, e.g. RNH_2 .
- Reactions of carboxylic acids, acid halides, anhydrides with alcohols and amines to make esters and amides; hydrolysis of esters and amides.
- Utility of Mg, Li, Cu, alkyl/aryl derivatives in synthesis of C–C bonds from, e.g. alkyl halides and carbonyl compounds.

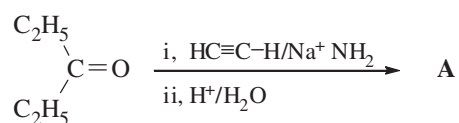
Question 3.25

Explain why the alcohol **3** cannot be prepared from cyclohexanone **4** using a Grignard reagent, and suggest an organometallic reagent that could be used to make compound **3** from **4**.



Question 3.26

Using curly arrows, draw a mechanism for the following nucleophilic addition reaction to show how the product **A** is formed, and hence deduce the structure of **A**.



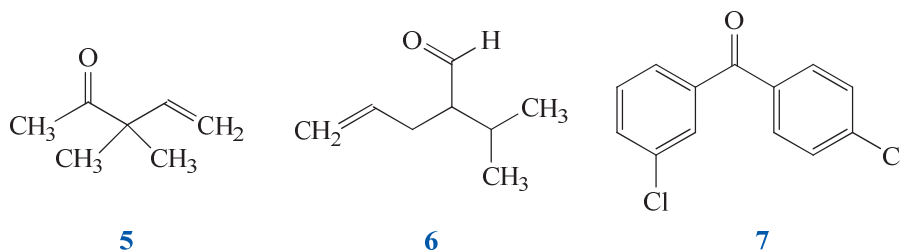
3.12 Organic synthesis and synthetic strategy

S315 draws on the following concepts and principles introduced in S215 Block 12 *Organic synthesis*.

- Basic principles of retrosynthetic analysis, i.e. working backwards from target molecule to starting materials.
- Disconnection strategy: C–X, C–C.
- Nucleophilic/electrophilic synthons and reagents.
- Functional group interconversions (FGI).
- Chemo-, regio- and stereoselectivity.
- Synthetic methodology in straightforward cases.
- Use of reagent tables.
- Protecting groups.

Question 3.27

Concentrating solely on the carbonyl groups, use retrosynthetic analysis to devise syntheses for compounds **5–7**, identifying the synthons and the corresponding reagents.



Question 3.28

- (a) Define the terms (i) chemoselectivity, (ii) regioselectivity and (iii) stereoselectivity, as applied to the reactions of organic compounds.
- (b) Briefly outline why protecting groups are sometimes required in organic synthesis?

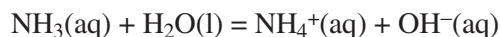
3.13 Main group chemistry

S315 draws on the following concepts and principles introduced in S215 Block 13 *Main group chemistry*.

- Polyprotic acids and pK_a .
- Reaction cycles.
- Conjugate acid/base.
- Ions in natural water.
- Amphoteric substances.
- Inert pair effect: influence on properties.
- Zeolites: polarity, acidity, porous structure, shape selective catalysts.
- Ammonia and the Haber–Bosch process.
- Polyphosphates such as ATP.

Question 3.29

Identify the conjugate acid-base pairs in the following reaction:



Question 3.30

Write down the equations that illustrate H_3PO_4 is a polyprotic acid.

Question 3.31

Aluminium(III) hydroxide is amphoteric and so dissolves in both acidic and basic solutions. Provide an equation to illustrate each of these reactions.

3.14 Biological concepts

The following concepts developed in Book 5 *Life* of S104 *Exploring science*, in particular Section 5.5 Proteins and Section 5.6 Enzymes, which introduce the basic principles of the structure and function of proteins and enzymes.

- The three fundamental attributes of living things; metabolism, growth and reproduction.
- The fundamental similarities between all organisms at the cellular and biochemical level.
- The differences between eukaryotic and prokaryotic cells.
- The biochemical building blocks of living things and the relationship between structure of a variety of biological molecules and the functions they carry out in the cell/organism.

- The importance to the cell/organism of metabolic processes including glucose oxidation and protein synthesis.
- Amino acids and formation of proteins from amino acid residues.
- Primary and higher order structure of proteins and protein binding sites.
- Basic features of enzymes.
- To recognise that enzymes are proteins that catalyse biochemical reactions, and all organisms rely on enzymic reactions for their survival.
- The basic structure of nucleic acids.

Question 3.32

Certain molecules found in cells often have hydrophilic and hydrophobic regions within their structure. Comment on how such a molecule would interact with water.

Question 3.33

- Draw the generalised structure of an amino acid.
- What is a peptide bond and how is it formed? Use a diagram to illustrate your answer.

Question 3.34

What is the function of enzymes in biological systems, and what is an 'active site'?

4 Mathematical skills

The level of mathematics required for S315 is not high; but to study the module successfully, you need to be comfortable and confident *using* a limited range of mathematical 'tools', particularly algebraic manipulation. These have been introduced in the Level 1 science modules S104 and S141 *Maths* (or S151 *Maths for Science*) and are used in S215.

The mathematical skills that are needed range from the simple calculation of double-bond equivalent, molar quantities and product yields, to the handling of equations, simple algebra, the powers of 10 and using logs, to the more complex plotting of data and using equations to calculate rate constants using the Graph plotter program (the program is introduced in S215). In addition, you must own and be able to use a scientific calculator.

4.1 Handling equations: simple algebra

The arguments and analyses in S315 often involve a series of simple algebraic manipulations. So you need to be familiar with the basic rules of algebra. In particular, you should be able to:

- Expand expressions that include brackets, and use brackets to simplify expressions.
- Add, subtract, multiply and divide fractions.
- Rearrange equations in order to simplify them or to change their subject.

- Substitute from one equation into another, in order to eliminate a particular quantity.
- Use powers to express roots and reciprocals, and combine powers in algebraic expressions.
- Use \log_{10} and natural logs and exponential terms.
- Recognise examples of direct and inverse proportionality.

Question 4.1

- (a) The ideal gas equation has the form $pV = nRT$ (where p is the pressure, V is the volume, n is the amount of gas (in moles), R is the gas constant and T is the temperature). Rearrange this equation to obtain an expression for the molar concentration, n/V .
- (b) The equilibrium constant K for a reaction is given by the equation $\ln K = -\Delta_m G^\ominus / RT$. Use the equation $\Delta_m G^\ominus = \Delta_m H^\ominus - T\Delta_m S^\ominus$ to eliminate $\Delta_m G^\ominus$.

Question 4.2

This question concerns the manipulation of expressions of the kind that are common in kinetics.

- (a) Rearrange the following equation:

$$k_1[A][C] - k_2[B] - k_3[A][B] = 0$$

to obtain an expression for the concentration of B, $[B]$.

- (b) Suppose that the concentration of A, $[A]$, varies with time t according to the equation:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

where $[A]_0$ is the initial concentration of A, and k is a constant. Rearrange this expression to make $[A]$ the subject of the equation (i.e. obtain an expression for $[A]$).

- (c) Suppose that the rate of a reaction is given by the expression

$$\text{rate} = k_1[A][B] \tag{1}$$

and that the concentrations of A and B are interrelated via the following equation:

$$k_2[A] - 2k_3[B]^2 = 0 \tag{2}$$

Use Equation 2 to obtain an expression for $[B]$, which you then substitute in Equation 1. Write the resulting expression for the rate in as simple a form as possible.

4.2 Handling data: tables, graphs and SI units

Plotting a graph is a very useful way of showing the relationship between two measured variables, or of testing whether a postulated relationship is valid. To study S315 successfully, you will need to handle tables of data that involve units and powers of ten, and to present analyses of such data in graphical form. The

course includes guidance in this area, but it would still be a good plan to check that you know how to:

- Give each column of data in a table an appropriate heading, or interpret correctly the heading provided.
- Plot a graph from a set of data, choosing an appropriate scale, and labelling the axes.
- Determine the slope and intercept of a straight-line graph, and hence obtain the equation that describes the line in terms of the standard form ($y = mx + c$).

Question 4.3

The mass M of a flask and its contents is measured as a function of the volume V of liquid in the flask; the results are given in Table 3.

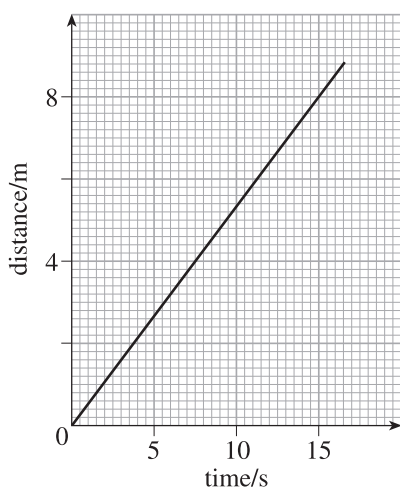
Table 3 Mass M of a flask and its contents as a function of the volume V of the liquid it contains.

$M/10^2$ g	$V/10^2$ cm ³
3.30	2.00
4.80	4.00
6.60	6.00
8.50	8.00
10.10	10.00

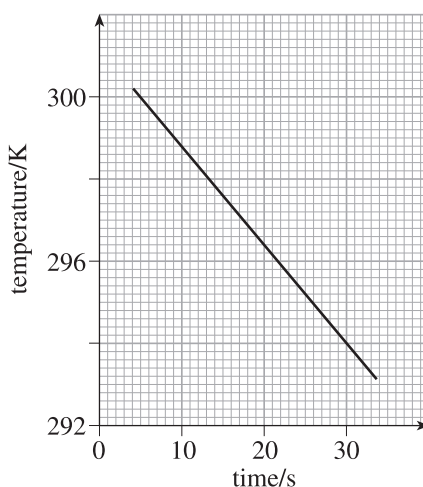
- (a) Consider the first row in Table 3:
- (i) what is the value of M in kg?
 - (ii) what is the value of V in m³?
- (b) Using the data in Table 3, plot a graph of M against V . Use your graph to determine the equation that relates M and V . What is the mass (M_0) of the empty flask?

Question 4.4

Determine the gradient of each of the straight lines in the graphs in Figure 4.



(a)



(b)

Figure 4 For use with Question 4.4.

4.3 Other mathematical skills

Relationships between physical quantities sometimes involve logarithms and/or exponentials, and kinetics uses the *language* of calculus to express the idea of a 'rate of change' in a precise way. S315 includes guidance in these areas, and this covers *all* of the points that you will need while studying the module. In particular, note that you will *not* be required to actually differentiate or integrate algebraic expressions during your study of S315.

5 Other skills

As a level 3 module it is assumed that you will already have the opportunity to develop the generic skills listed below.

- Time management skills;
- Effective reading to extract relevant from irrelevant or redundant information and data from scientific texts, diagrams, graphs and accounts;
- Drawing logical conclusions and inferences from data presented in various formats;
- Summarising selected information in your own words;
- Constructing logical, coherent and objective arguments;
- Structuring and writing a short scientific account, illustrated with suitable diagrams (if appropriate).
- Use of a computer and the internet to obtain information;
- Use of molecular drawing software such as Accelrys Draw or ACD ChemSketch (and JSME in activities);
- Use of JSMol for molecular visualisation;
- Use of the word processing and data handling software programs.

If you need to read about the tips and guidance on effective study you can visit the 'Skills for OU Study' and the Library websites. Both can be accessed from your StudentHome.

6 Answers to the self-assessment questions

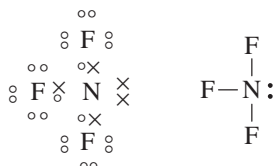
Question 3.1

- (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^1$: main group element in Group III (outer electron configuration is $s^2 p^1$)
 (ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$: transition element (partially filled d shell)
 (iii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$: main group element in Group 0 (a noble gas; outer electron configuration is $s^2 p^6$).
- (b) Group VII (F, Cl, Br, I, At). The electronegativity is a measure of the power of an atom to attract electrons to itself when entering into chemical combination. On moving across a Period, this is most affected by the increase in nuclear charge.
- (c) The second Period (Li, Be, B, C, N, O, F). The small size predominates over the increase in the nuclear charge on moving down a Group.

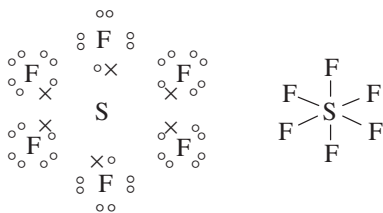
Question 3.2

- (a) (i) Ionic bonding (i.e. a regular three-dimensional array of Ca^{2+} ions and F^- ions in the ratio 1 : 2);
 (ii) extended covalent array;
 (iii) metallic bonding.

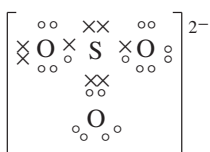
(b) NF_3



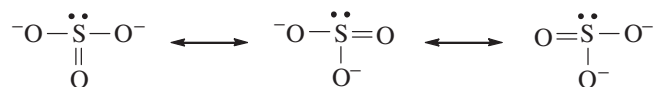
SF_6



SO_3^{2-}



For SO_3^{2-} there are three resonance hybrids:



Question 3.3

- (a) Chromium +6 in $\text{Cr}_2\text{O}_7^{2-}$; vanadium +4 in VO^{2+} ; chromium +3 in CrO_2^- ; chromium +6 in CrO_4^{2-} ; chlorine +1 in ClO^- .
- (b) (i) $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) + 6\text{V}^{3+}(\text{aq}) = 2\text{Cr}^{3+}(\text{aq}) + 6\text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
(ii) $3\text{ClO}^-(\text{aq}) + 2\text{CrO}_2^-(\text{aq}) + 2\text{OH}^-(\text{aq}) = 3\text{Cl}^-(\text{aq}) + 2\text{CrO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- (c) (i) Chromium is reduced from an oxidation state of +6 to +3; vanadium is oxidised from oxidation state +3 to +4.
(ii) Chlorine is reduced from an oxidation state of +1 to -1; chromium is oxidised from oxidation state +3 to +6.

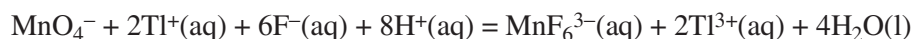
Question 3.4

The number of moles of MnO_4^- is $0.025 \text{ mol dm}^{-3} \times \frac{20 \text{ dm}^3}{1000}$
 $= 5 \times 10^{-4} \text{ mol}$ (since $1 \text{ dm}^3 = 1000 \text{ cm}^3$).

The number of moles of Tl^+ is $0.1 \text{ mol dm}^{-3} \times \frac{10 \text{ dm}^3}{1000} = 1 \times 10^{-3} \text{ mol}$

Therefore, the ratio of $\text{Tl}^+:\text{MnO}_4^- = 1 \times 10^{-3} : 5 \times 10^{-4} = 0.001 : 0.0005 = 2 : 1$.

The thallium changes oxidation state by +2. If two moles of thallium(I) are needed to reduce 1 mole of MnO_4^- , then the oxidation state of the manganese must change by $2 \times 2 = 4$. In MnO_4^- the manganese is in oxidation state +7, therefore in the product it is $+(7 - 4) = +3$. The reaction is represented by the equation:



Question 3.5

Arrhenius: An acid is a substance that contains hydrogen and when dissolved in water releases hydrogen ions, $\text{H}^+(\text{aq})$. A base is a compound that gives hydroxide ions, $\text{OH}^-(\text{aq})$, when dissolved in water.

Brønsted–Lowry: An acid is a substance from which a proton can be removed. A base is a substance that can accept a proton from an acid.

Lewis: A Lewis acid can accept a non-bonding pair of electrons. A Lewis base donates a non-bonding pair of electrons.

Question 3.6

The nitrogen $2p_z$ orbitals overlap to form a bonding orbital $2p\sigma_g$ (lower energy than the atomic orbitals from which it was constructed) and an antibonding $2p\sigma_u$ (higher energy than the atomic orbitals from which it was made).

The nitrogen $2p_x$ and $2p_y$ orbitals overlap to form two degenerate (equal energy) pairs of molecular orbitals, labelled $2p\pi_u$ (bonding) and $2p\pi_g$ (antibonding).

Recall, for molecules with a centre of symmetry (and atoms), the orbitals can be labelled based on whether they appear identical or as their negative (phase) when inverted through the centre of symmetry of the molecule. Those orbitals that appear identical are given the label 'g' (standing for *gerade*, German for even),

and those that change sign are given the label 'u' (standing for *ungerade*, German for odd).

The bond order is equal to the number of electrons in bonding orbitals minus the number of electrons in antibonding orbitals divided by 2.

For dinitrogen, the bond order is $(6 - 0)/2 = 3$, and so N_2 has a triple bond.

All the electrons are paired and so N_2 is diamagnetic.

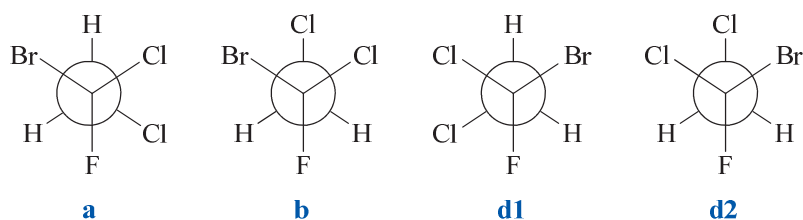
Question 3.7

(a) Molecules **a** and **d** are stereoisomers, since the atoms are all joined together in exactly the same sequence. They are non-superimposable mirror images, so they are enantiomers. However much we rotate the molecules about the C–C bonds, we can never make **a** and **d** identical. Molecules **b** and **d** are also enantiomers.

(b) Molecules **a** and **b** have the same configurations around the chiral carbons, since the arrangement of Br, Cl and F atoms is identical.

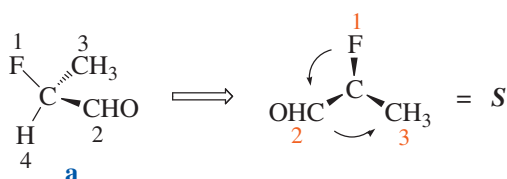
Compound **c** contains the same atoms as **a**, **b** and **d**, but they are arranged in a different order. Compound **c** is therefore a structural isomer (positional isomer) of **a**, **b** and **d** because it has the same molecular formula, $C_2H_2BrCl_2F$, as the other molecules, but a different ordering of the atoms.

Newman projections of **a**, **b** and **d** show clearly that **a** is the mirror image of **d1** and **b** the mirror image of **d2**. Newman projection **d2** is generated by rotating the rear carbon atom of **d1** clockwise through 120° .

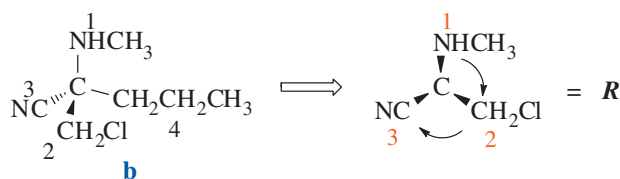


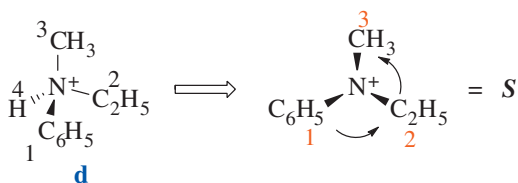
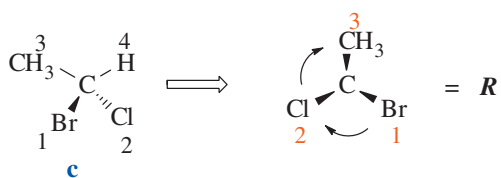
(c) **a** and **b** can easily be made identical by rotation about the C–C bond, and are therefore different conformations of the same molecule.

Question 3.8



The priority order for this molecule is: $F > CHO$ (carbon attached to oxygen and hydrogen) $> CH_3$ (carbon attached only to hydrogen) $> H$. The priorities are shown above for when the molecule is reorientated.

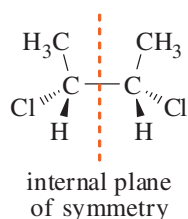




Structure **d** is interesting, in that it shows that not just *carbon* centres with four different groups attached are chiral. Appropriately substituted ammonium ions can also exhibit chirality.

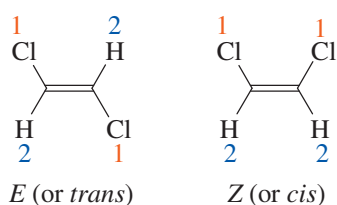
Question 3.9

A *meso* compound contains chiral centres but it is not itself chiral. It has an internal plane of symmetry and therefore does not rotate the plane of plane-polarised light.

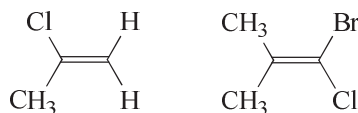


Question 3.10

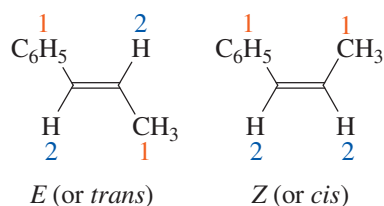
(a) $\text{ClHC}=\text{CHCl}$ has two isomers:



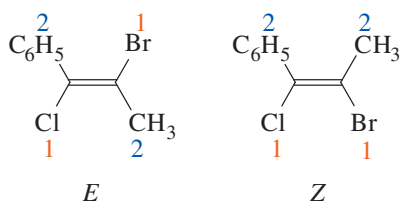
(b) and (c) There is only one $\text{Cl}(\text{CH}_3)\text{C}=\text{CH}_2$, and one $(\text{CH}_3)_2\text{C}=\text{CBrCl}$, so the labels *cis* and *trans*, or *E* and *Z*, are not applicable.



(d) $(\text{C}_6\text{H}_5)\text{HC}=\text{CHCH}_3$ has two isomers:

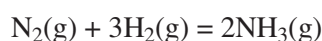


- (e) $(\text{C}_6\text{H}_5)\text{ClC}=\text{CBrCH}_3$ has two isomers, but the labels *cis* and *trans* are not appropriate (as the four groups are all different), whereas *E* and *Z* are easily applied.



Question 3.11

- (a) Remember that values of $\Delta_{\text{m}}H^{\ominus}$, $\Delta_{\text{m}}G^{\ominus}$, $\Delta_{\text{m}}S^{\ominus}$ and K are all linked to the specified balanced chemical equation. In this case:



$$\begin{aligned} \text{(i)} \quad \Delta_{\text{m}}H^{\ominus} &= 2\Delta_{\text{f}}H^{\ominus}(\text{NH}_3, \text{g}) - \Delta_{\text{f}}H^{\ominus}(\text{N}_2, \text{g}) - 3\Delta_{\text{f}}H^{\ominus}(\text{H}_2, \text{g}) \\ &= \{2 \times (-46.0) - 0 - 0\} \text{ kJ mol}^{-1} = -92.0 \text{ kJ mol}^{-1} \end{aligned}$$

Since $\Delta_{\text{m}}H^{\ominus} < 0$ (i.e. negative), the reaction is exothermic.

$$\text{(ii)} \quad \text{Use } \Delta_{\text{m}}G^{\ominus} = \Delta_{\text{m}}H^{\ominus} - T\Delta_{\text{m}}S^{\ominus}$$

$$\begin{aligned} \Delta_{\text{m}}S^{\ominus} &= 2S^{\ominus}(\text{NH}_3, \text{g}) - S^{\ominus}(\text{N}_2, \text{g}) - 3S^{\ominus}(\text{H}_2, \text{g}) \\ &= \{(2 \times 192.5) - 191.6 - (3 \times 130.7)\} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -198.7 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(Note that the absolute entropies of the elements are **not** zero.)

$$\Delta_{\text{m}}H^{\ominus} = -92.0 \text{ kJ mol}^{-1} \text{ (from part (i)), so}$$

$$\begin{aligned} \Delta_{\text{m}}G^{\ominus} &= (-92.0 \text{ kJ mol}^{-1}) - (298.15 \text{ K}) \times (-198.7 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= (-92.0 + 59.24) \text{ kJ mol}^{-1} = -32.8 \text{ kJ mol}^{-1} \end{aligned}$$

(Note the factor of 10^{-3} which converts the value of $\Delta_{\text{m}}S^{\ominus}$ from $\text{J K}^{-1} \text{ mol}^{-1}$ into $\text{kJ K}^{-1} \text{ mol}^{-1}$.)

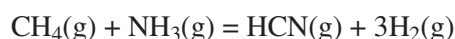
Since $\Delta_{\text{m}}G^{\ominus} < 0$, the reaction is thermodynamically favourable at 298.15 K.

$$\text{(iii)} \quad K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

With concentrations measured in mol dm^{-3} , the unit of K would be:

$$(\text{mol dm}^{-3})^2 \text{ }^{-1} \text{ }^{-3} = (\text{mol dm}^{-3})^{-2} \text{ or } \text{mol}^{-2} \text{ dm}^6$$

- (b) For the reaction:



At 298.15 K,

$$\begin{aligned} \Delta_{\text{m}}H^{\ominus} &= \Delta_{\text{f}}H^{\ominus}(\text{HCN}, \text{g}) + 3\Delta_{\text{f}}H^{\ominus}(\text{H}_2, \text{g}) - \Delta_{\text{f}}H^{\ominus}(\text{CH}_4, \text{g}) - \Delta_{\text{f}}H^{\ominus}(\text{NH}_3, \text{g}) \\ &= \{135.1 + 3(0) - (-74.8) - (-46.0)\} \text{ kJ mol}^{-1} \\ &= (135.1 + 74.8 + 46.0) \text{ kJ mol}^{-1} = 255.9 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta_{\text{m}}S^{\ominus} &= S^{\ominus}(\text{HNC, g}) + 3S^{\ominus}(\text{H}_2, \text{g}) - S^{\ominus}(\text{CH}_4, \text{g}) - S^{\ominus}(\text{NH}_3, \text{g}) \\ &= \{201.8 + 3(130.7) - 186.3 - 192.5\} \text{ J K}^{-1}\text{mol}^{-1} \\ &= 215.1 \text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Assuming that the values of $\Delta_{\text{m}}H^{\ominus}$ and $\Delta_{\text{m}}S^{\ominus}$ do not vary with temperature (which is reasonable if there is no change of phase), and using $\Delta_{\text{m}}G^{\ominus} = \Delta_{\text{m}}H^{\ominus} - T\Delta_{\text{m}}S^{\ominus}$, at 473.15 K:

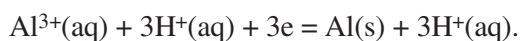
$$\begin{aligned}\Delta_{\text{m}}G^{\ominus} &= (255.9 \text{ kJ mol}^{-1}) - (473.15 \text{ K}) \times (215.1 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1}) \\ &= 154.1 \text{ kJ mol}^{-1}\end{aligned}$$

Since $\Delta_{\text{m}}G^{\ominus} > 0$, the reaction is not thermodynamically favourable at 473.15 K.

Question 3.12

Standard redox potentials are reduction potentials by definition, so the equation must be transposed from right to left. For this reaction $\Delta_{\text{m}}G^{\ominus} = 485 \text{ kJ mol}^{-1}$.

To obtain the equation in the usual form, you must recognise that $\frac{1}{2}\text{H}_2(\text{g}) = \text{H}^+ + \text{e}$ (where e = an electron). Therefore the equation becomes:



Eliminating the H^+ from both sides of the equation gives $\text{Al}^{3+}(\text{aq}) + 3\text{e} = \text{Al}(\text{s})$.

Now $\Delta_{\text{m}}G^{\ominus} = -nFE^{\ominus}$. Therefore

$$\begin{aligned}485 \times 10^3 \text{ J mol}^{-1} &= (-3 \times 96\,485 \text{ C mol}^{-1}) E^{\ominus} \\ \text{that is, } E^{\ominus} &= -1.68 \text{ V} \\ (1 \text{ V} &= 1 \text{ J C}^{-1})\end{aligned}$$

(b) As $E^{\ominus}(\text{Al}^{3+} | \text{Al}) = -1.68 \text{ V}$, it is a relatively high negative potential (cf. $E^{\ominus}(\text{Zn}^{2+} | \text{Zn}) = -0.76 \text{ V}$ and $E^{\ominus}(\text{Mg}^{2+} | \text{Mg}) = -2.36 \text{ V}$), so aluminium is expected to be a powerful reducing agent.

Question 3.13

The kinetic reaction profile for the reaction of $(\text{CH}_3)_2\text{CHBr}$ with excess potassium hydroxide, drawn using the Graph plotter should be similar to Figure A1, in which a smooth curve is fitted through the data points.

Using the method of half-lives:

At $t = 0 \text{ s}$ $[(\text{CH}_3)_2\text{CHBr}]_0 = 150 \times 10^{-3} \text{ mol dm}^{-3}$.

A preliminary check for first-order behaviour requires that successive half-lives are measured.

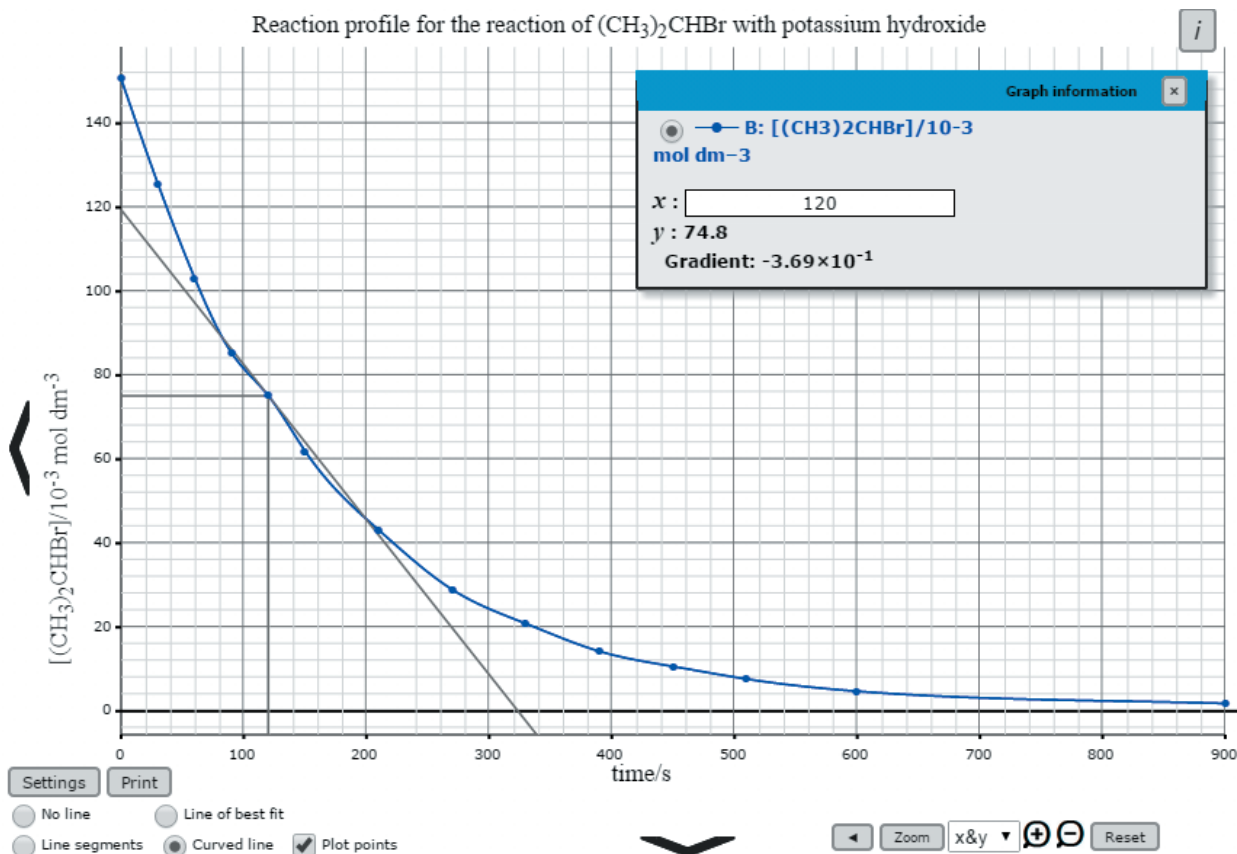


Figure A1 Reaction profile for the reaction of $(\text{CH}_3)_2\text{CHBr}$ with potassium hydroxide.

Using the Graph plotter, it is possible to obtain four half-lives from the plot by positioning the cursor on the smooth curve so that:

$$t_{1/2}(1) \text{ is when } [(\text{CH}_3)_2\text{CHBr}]_0 \text{ falls to } [(\text{CH}_3)_2\text{CHBr}]_0 \approx 120 \text{ s}$$

$$t_{1/2}(2) \text{ is when } [(\text{CH}_3)_2\text{CHBr}]_0 \text{ falls to } \frac{1}{4} [(\text{CH}_3)_2\text{CHBr}]_0 \approx 110 \text{ s}$$

$$t_{1/2}(3) \text{ is when } \frac{1}{4} [(\text{CH}_3)_2\text{CHBr}]_0 \text{ falls to } \frac{1}{8} [(\text{CH}_3)_2\text{CHBr}]_0 \approx 114 \text{ s}$$

$$t_{1/2}(4) \text{ is when } \frac{1}{8} [(\text{CH}_3)_2\text{CHBr}]_0 \text{ falls to } \frac{1}{16} [(\text{CH}_3)_2\text{CHBr}]_0 \approx 122 \text{ s}$$

Clearly, the four successive half-lives are equal to one another, given the experimental errors in kinetic experiments, so the reaction is likely to be first-order with respect to $(\text{CH}_3)_2\text{CHBr}$. In this reaction, potassium hydroxide was present in excess. Therefore it is a pseudo first-order reaction.

Question 3.14

The activation energy can be derived using the Arrhenius equation which takes the form:

$$k_R = A \exp\left(-\frac{E_a}{RT}\right)$$

Taking natural logs and rearranging the equation:

$$\ln k_R = -\frac{E_a}{RT} + \ln A$$

This is the equation for a straight line, so a plot of $\ln k_R$ versus $1/T$ should be linear (Figure A2). This assumes that both A and E_a are constants, independent of temperature, which is reasonable for most reactions when studied over a limited temperature range.

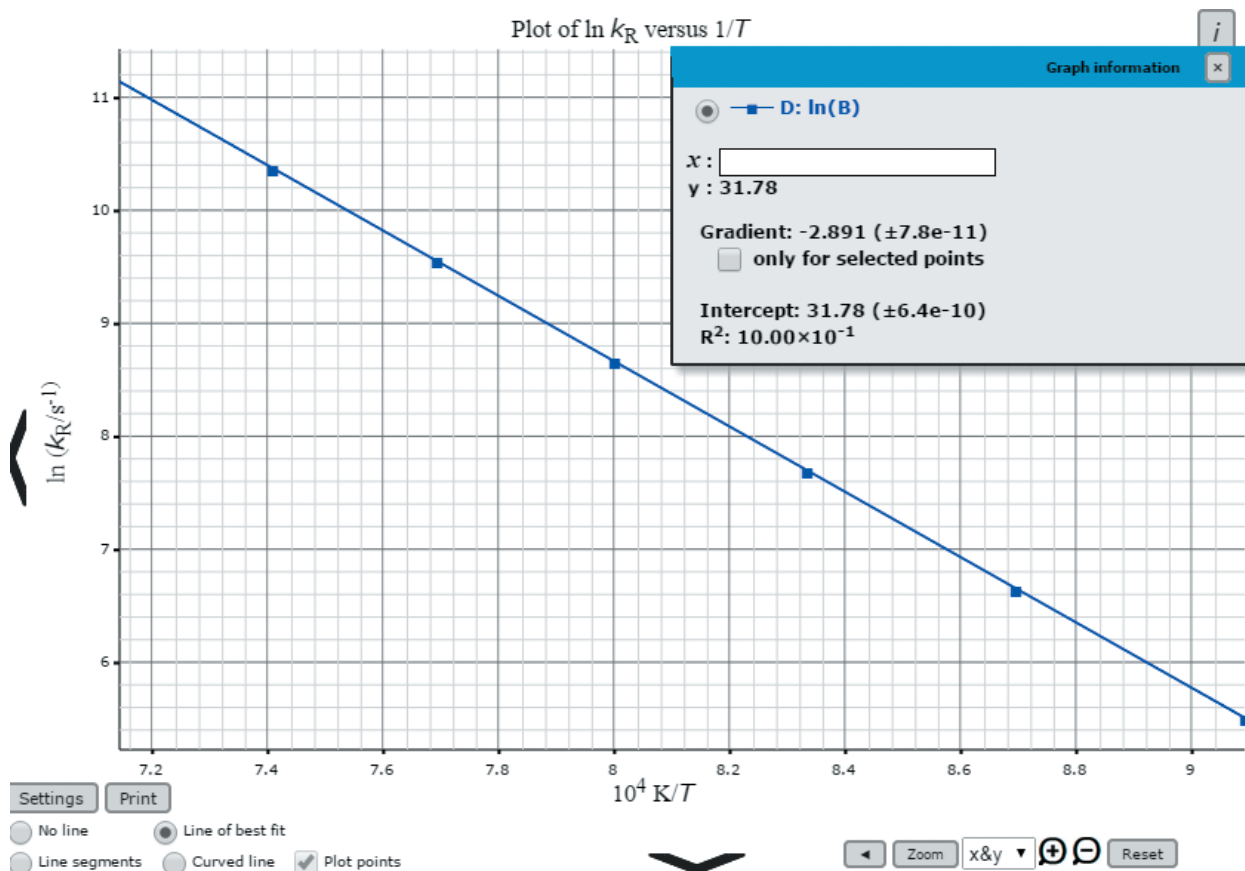


Figure A2 An Arrhenius plot of $\ln k_R$ versus $1/T$ for the decomposition of chloroethane.

The gradient = $-E_a/R = -2.89 \times 10^4 \text{ K}$

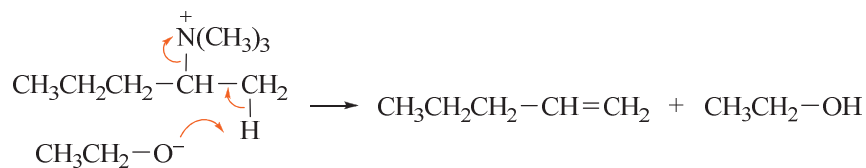
Thus, $E_a = 2.89 \times 10^4 \text{ K} \times 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$
 $= 240 \text{ kJ mol}^{-1}$

Question 3.15

- The reaction of a primary substrate with a good nucleophile, such as iodide, would be expected to go by an S_N2 mechanism. However, chloride is also a good nucleophile, and an equilibrium would be expected.
- Once again, the S_N2 mechanism is expected with a primary substrate and a good nucleophile.
- This reaction would almost certainly proceed exclusively by an S_N1 mechanism. All the conditions (a tertiary substrate, a fairly poor nucleophile) favour this mechanism.
- Secondary substrates can react by either the S_N1 or the S_N2 mechanism. However, the use of a good nucleophile, in high concentration should favour the S_N2 mechanism.

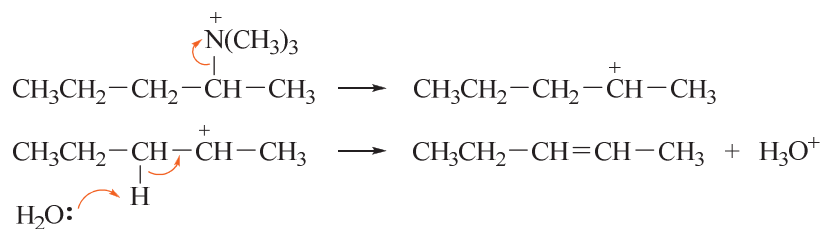
Question 3.16

(a) Reaction with sodium ethoxide via an E2 mechanism is shown below:



Hoffman's rule suggests the least substituted alkene will be formed because of the charged leaving group.

(b) Reaction with water via an E1 mechanism is shown below:



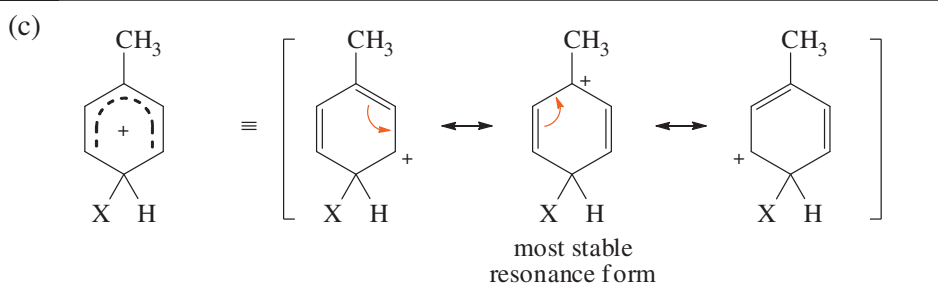
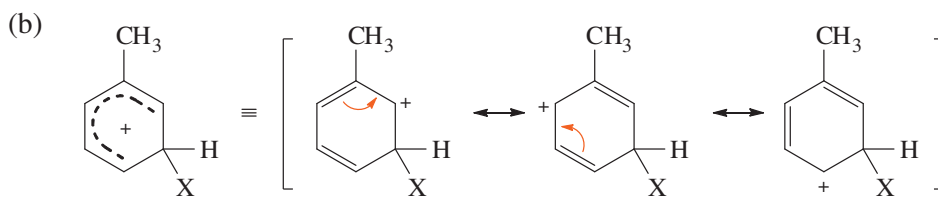
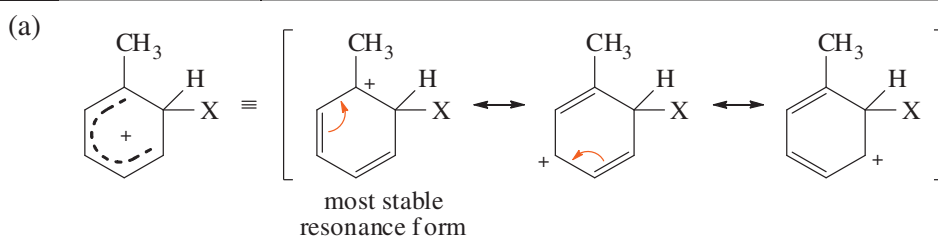
E1 reactions usually obey Saytzev's rule to give the more substituted alkene. Since the more stable alkene is formed the *E* form predominates.

Question 3.17

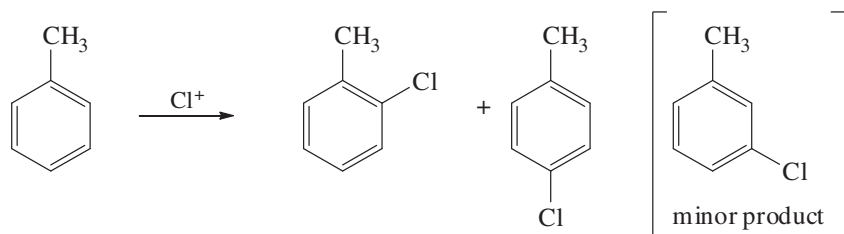
The resonance form for the carbocations formed in this electrophilic aromatic substitution are shown below:

delocalised
intermediate
carbocation

resonance forms

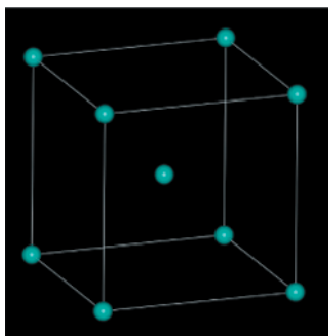


- (d) This is an electrophilic aromatic substitution reaction. The electrophile is Cl^+ . The CH_3 group on methylbenzene has 1,4-directing effect (*ortho/para*, with stabilised resonance form of tertiary carbocation). Therefore the major products are 1-chloro-2-methylbenzene and 1-chloro-4-methylbenzene.

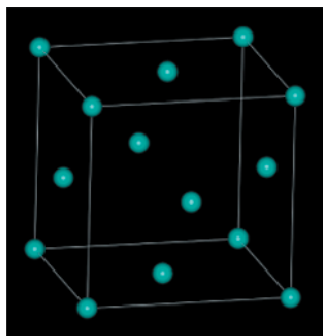


Question 3.18

- (a) A body-centred cubic lattice:



A face-centred cubic lattice:



- (b) The body-centred cell has $(8 \times \frac{1}{8})$ atoms at the corners and one atom in the centre (which is not shared), making 2 atoms in total.

For the face-centre cubic cell, the face is shared by two unit cells. Therefore, the face-centred cell has $(6 \times \frac{1}{2})$ atoms on the faces and $(8 \times \frac{1}{8})$ at the corners, making a total of 4 atoms.

Question 3.19

- (a) $\lambda = c/v$ and $\sigma = 1/\lambda$.

For 1.216×10^{10} Hz:

$$\lambda = (3 \times 10^8 \text{ m s}^{-1}) / (1.216 \times 10^{10} \times 10^{-3} \text{ s}^{-1}) = 2.467 \times 10^{-2} \text{ m},$$

$$\text{And } \sigma = 1 / (2.467 \text{ cm}) = 0.4054 \text{ cm}^{-1}.$$

$$\text{For } 2.580 \times 10^{13} \text{ Hz: } \lambda = (3 \times 10^8 \text{ m s}^{-1}) / (2.580 \times 10^{13} \text{ Hz}) = 1.163 \times 10^{-5} \text{ m}$$

$$\text{And } \sigma = 1 / (1.163 \times 10^{-3} \text{ cm}) = 859.8 \text{ cm}^{-1}.$$

- (b) The absorption at 1.216×10^{-10} Hz is in the microwave region, and that at 2.580×10^{13} Hz is in the infrared region.
- (c) The microwave transition is likely to be caused by a rotational change, and the infrared transition will be caused by a vibrational change in the molecule.

Question 3.20

- (a) Only those molecules in which the dipole moment changes during the vibration are infrared active: these are the heteronuclear molecules HF, HCl and NO.
- (b) Molecules that change their polarisability during vibration are active in the Raman spectrum. All diatomic molecules do this, so the vibrations of all the molecules are Raman active.

Question 3.21

The molecular formula is $C_6H_{14}O$, so the compound has no double-bond equivalents. It is fully saturated and acyclic.

The NMR spectrum (Figure 2)

- (i) There are six signals, corresponding to six magnetically non-equivalent carbon atoms, so there is no equivalence. All except the signal at 75 p.p.m. are in the aliphatic region.
- (ii) CH_3 q at about 11 p.p.m.
 CH_3 q at about 15 p.p.m.
 CH_2 t at about 20 p.p.m.
 CH_2 t at about 32 p.p.m.
 CH_2 : t at about 39 p.p.m.
 CH d at about 75 p.p.m.; its chemical shift suggests CH–O.

The infrared spectrum (Figure 3)

C–H stretch at just below 3000 cm^{-1} , saturated aliphatic

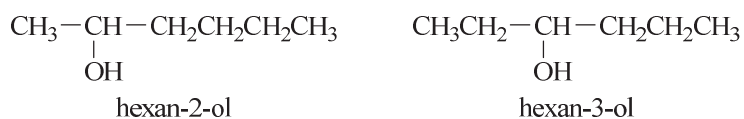
Broad O–H stretch at $\approx 3370\text{ cm}^{-1}$, alcohol

No C=C stretch near 1600 cm^{-1} , not an alkene

No C=C–H stretch above 3000 cm^{-1} , not an alkene

No C=O stretch near 1700 cm^{-1} , not a carbonyl compound

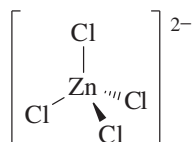
There are two possible structures:



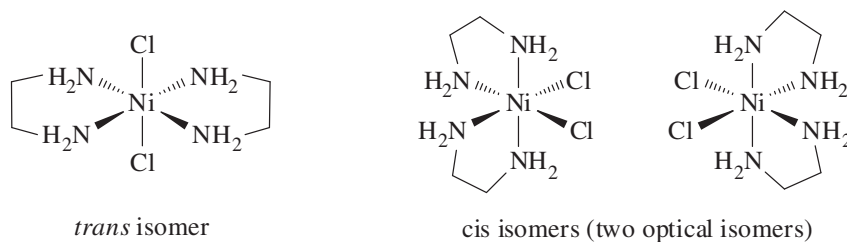
It is not possible to distinguish between these two structures on the basis of the spectral data given.

Question 3.22

- (a)



(b) The ethylenediamine is a bidentate ligand and the complexes are octahedral.



Question 3.23

- (a) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ Cr(III) $3d^3$
 (b) $[\text{CoCl}_4]^{2-}$ Co(II) $3d^7$
 (c) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ Pt(II) $5d^8$

Question 3.24

(a) The energy level diagram for a transition-metal in an octahedral field is shown in Figure A3.

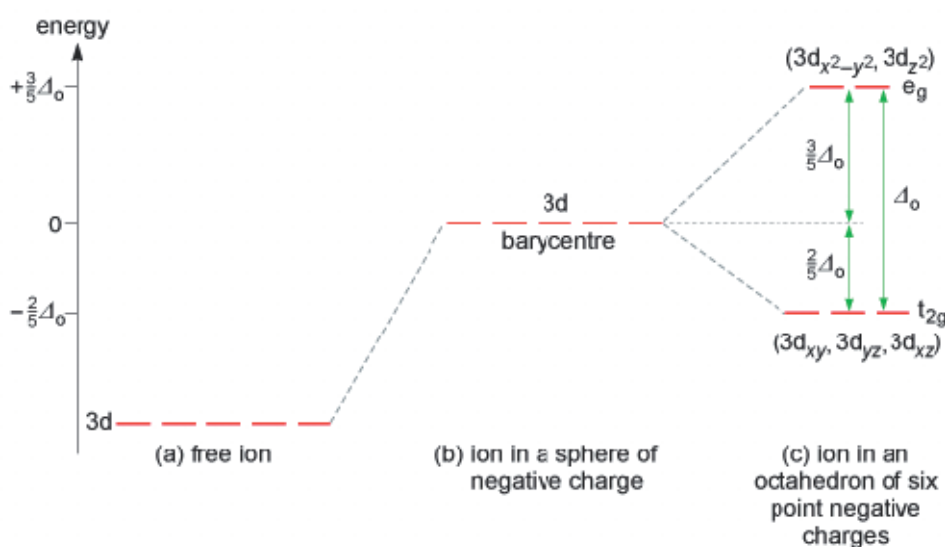


Figure A3 Partial orbital energy-level diagram showing the 3d levels only of a transition-metal ion for: (a) a free ion; (b) an ion in a sphere of negative charge; (c) an ion in an octahedron of six point negative charges.

(b) A d^5 transition metal has 5 electrons. In a weak field, or high-spin case, the gap Δ_o is small and so electrons enter the orbitals of the upper level when the lower level is full of electrons of one spin. In a strong field, or low-spin case, the energy gap Δ_o is large and the electrons pair up in the lower level before entering the upper level. This is illustrated in Figure A4.

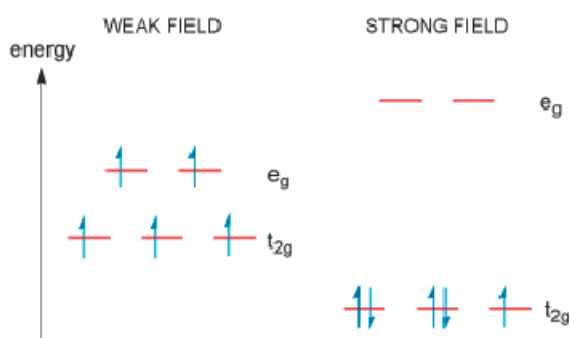
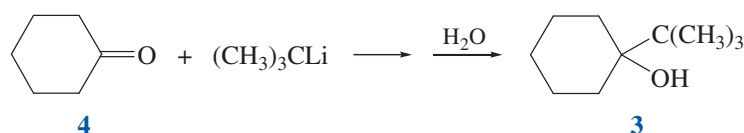


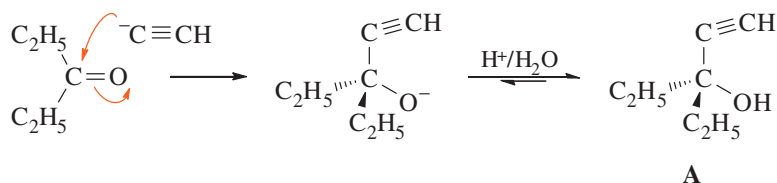
Figure A4 Occupation of 3d orbitals for d^5 complexes in weak and strong octahedral crystal fields.

Question 3.25

The appropriate Grignard reagent $(\text{CH}_3)_3\text{CMgBr}$ is bulky, and its approach to the carbonyl group of cyclohexanone (**4**) would be impeded by the C–H bonds in the ring; that is, reaction of cyclohexanone with 1,1-dimethylethylmagnesium bromide is sterically hindered. The corresponding organolithium compound is the reagent of choice:

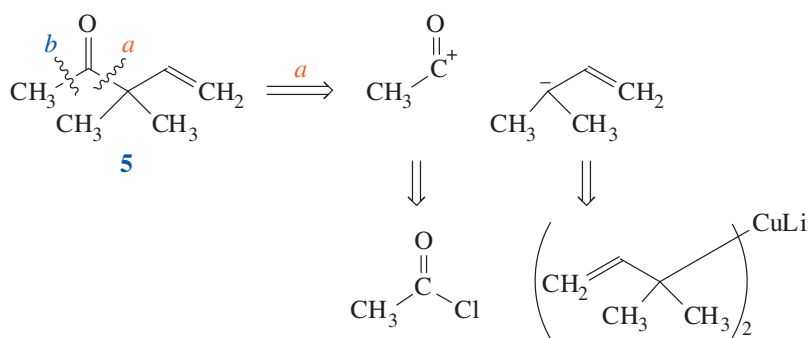


Question 3.26



Question 3.27

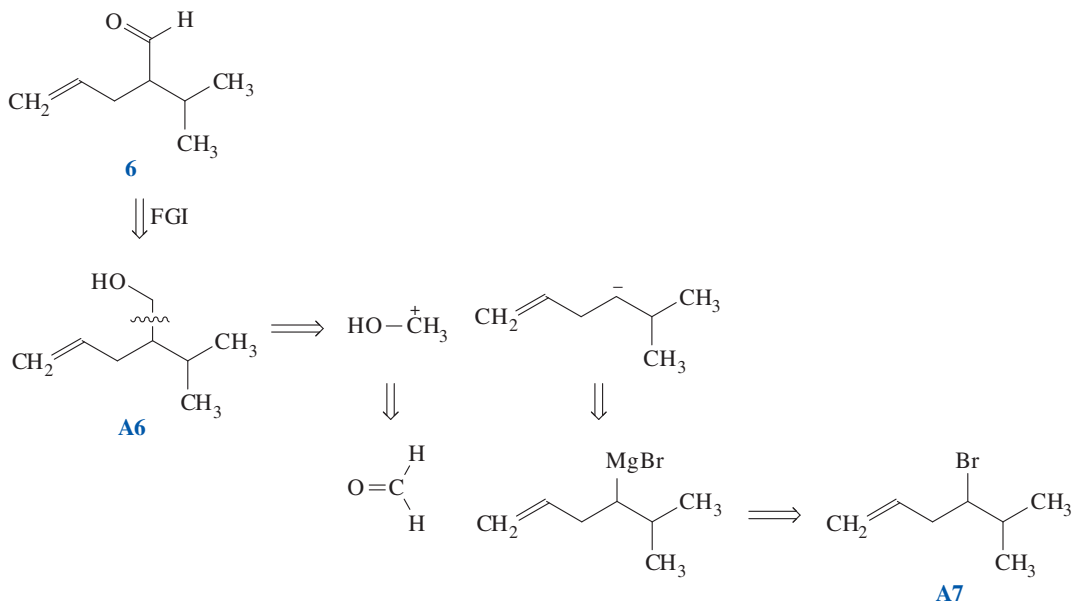
Compound **5** may be disconnected at *a* or *b*, but disconnection *a* simplifies the strategy more, so this is the disconnection of choice:



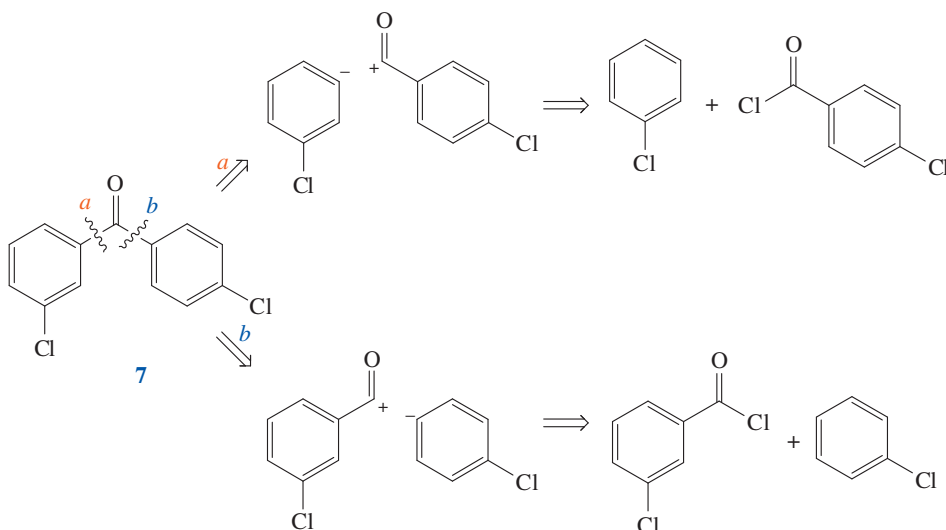
This strategy identifies a carbonyl electrophile, such as ethanoyl chloride, and an organometallic nucleophile, such as a lithium dialkylcopper compound.

Alternatively, ethanenitrile, CH_3CN , and the appropriate alkyl Grignard reagent would be suitable reagents.

Compound **6** is an aldehyde, which is analysed by carrying out first a functional group interconversion (FGI) to the corresponding alcohol, **A6**. The Grignard reagent can be made from 4-bromo-5-methylhex-1-ene (**A7**). For the final synthesis step of **6**, oxidation of alcohol **A6** may be achieved using pyridine– CrO_3 – HCl .

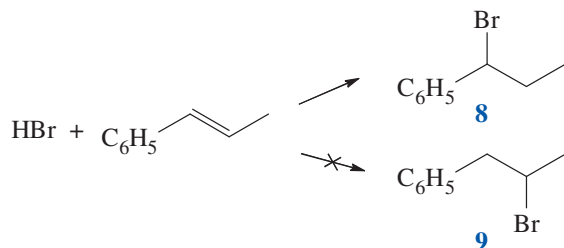


Compound **7** could be disconnected at either *a* or *b*. Disconnection *a* is derived from the Friedel–Crafts acylation of chlorobenzene with 4-chlorobenzoyl chloride, whereas disconnection *b* identifies the similar acylation of chlorobenzene with 3-chlorobenzoyl chloride. In the former, the acylation must occur in the *meta*-position of chlorobenzene. In the latter, it is the *para*-position of chlorobenzene that must be acylated. As the chlorine atom is *ortho/para*-directing, it is the approach identified by disconnection *b* that provides a suitable synthesis.

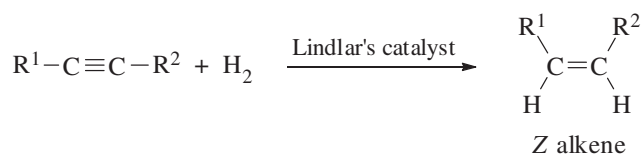


Question 3.28

- (a) (i) chemoselectivity The type of selectivity that arises because of a difference in reactivity between two *functional groups*, and in which reaction is effected at the more reactive of the two sites.
- (ii) regioselectivity A reaction is regioselective if it occurs preferentially at one site within the molecule (where reaction at more than one site is possible). For example, the addition of HBr to the alkene is regioselective, because reaction takes place preferentially to form **8**, rather than the other possible product, **9**.



- (iii) stereoselective A reaction is stereoselective if one *stereoisomer* is formed preferentially when the formation of more than one *stereoisomer* is possible. The hydrogenation of an alkyne using Lindlar's catalyst is an example of a stereoselective reaction, because in such a reduction only the *Z* alkene is formed.

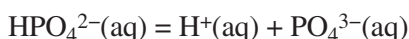
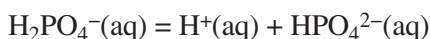
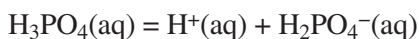


- (b) A protecting group is used to convert a functional group temporarily into a different functional group that will not react under the conditions of the transformation that is being attempted. Protecting groups must be easily removable (deprotection) once the desired transformation has been successfully completed.

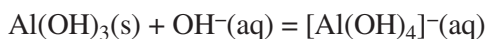
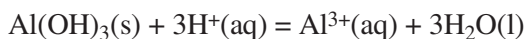
Question 3.29

H₂O is one acid; OH⁻ is its conjugate base. The other acid–base pair is NH₄⁺/NH₃.

Question 3.30



Question 3.31

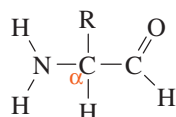


Question 3.32

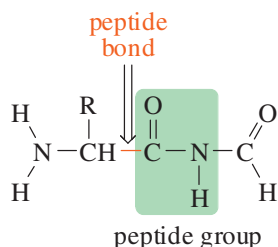
The hydrophilic groups would interact with water, but the hydrophobic groups would interact with one another i.e. avoid water as far as possible, this determines the molecule's three dimensional structure in water.

Question 3.33

- (a) The generalised structure of an amino acid is shown below, where R is the variable side chain. The C_α carbon is linked to an amino group, a carboxylic acid group and a side chain.



- (b) A peptide bond is the bond formed between two amino acid residues in a polypeptide. It is formed by the elimination of a water molecule between the amino group of one amino acid and the carboxyl group of another. The atoms within the box comprise the peptide group.



Question 3.34

Enzymes are highly selective biological catalysts that participate in a vast number of reactions in living systems. The active site is the point on the enzyme at which a substrate binds and undergoes chemical modification

Question 4.1

- (a) According to the ideal gas equation

$$pV = nRT$$

So $p = nRT/V$ (dividing both sides by V)

or $p/RT = n/V$ (dividing both sides by RT)

- (b) $\ln K = -\Delta_m G^\ominus / RT$ and $\Delta_m G^\ominus = \Delta_m H^\ominus - T\Delta_m S^\ominus$

Substituting for $\Delta_m G^\ominus$, the first expression becomes:

$$\ln K = -\frac{(\Delta_m H^\ominus - T\Delta_m S^\ominus)}{RT} = -\frac{\Delta_m H^\ominus}{RT} + \frac{\Delta_m S^\ominus}{R}$$

Question 4.2

- (a) $k_1[A][C] - k_2[B] - k_3[A][B] = 0$

Using brackets to collect the terms in $[B]$, this becomes:

$$k_1[A][C] - [B](k_2 + k_3[A]) = 0$$

So $k_1[A][C] = [B](k_2 + k_3[A])$ (adding $[B](k_2 + k_3[A])$ to both sides)

$$\text{And } [B] = \frac{k_1[A][C]}{(k_2 + k_3[A])} \text{ (dividing both sides by the term in brackets)}$$

- (b) Both sides of an equation can be inverted (i.e. you can take the reciprocal of each side) and the resulting terms will also be equal. But you need to take care when there is more than one term on one side of the equation, as in this example. A reliable strategy is as follows:

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt = \frac{1}{[A]_0} + \frac{kt[A]_0}{[A]_0} = \frac{1 + kt[A]_0}{[A]_0}$$

Inverting each side then gives:

$$[A] = \frac{[A]_0}{1 + kt[A]_0} \text{ (not } [A]_0 + \frac{1}{kt} \text{)}$$

$$(c) \quad k_2[A] - 2k_3[B]^2 = 0 \quad (2)$$

So $k_2[A] = 2k_3[B]^2$ (adding $2k_3[B]^2$ to both sides)

or $[B]^2 = k_2[A]/2k_3$ (dividing both sides by $2k_3$)

So $[B] = (k_2[A]/2k_3)^{1/2}$ (taking the square root of each side)

Substituting this expression for $[B]$ in Equation 1 then gives:

$$\begin{aligned} \text{rate} &= k_1[A][B] = k_1[A] \left(\frac{k_2[A]}{2k_3} \right)^{1/2} \\ &= k_1 \left(\frac{k_2}{2k_3} \right)^{1/2} [A][A]^{1/2} \\ &= k_1 \left(\frac{k_2}{2k_3} \right)^{1/2} [A]^{3/2} \end{aligned}$$

Question 4.3

- (a) (i) The entries in the first column of Table 3 are the numerical values of the quantity that appears as the heading to this set of data. So for the first entry:

$$M/10^2 \text{ g} = 3.30$$

$$\text{So } M = 3.30 \times 10^2 \text{ g}$$

$$= 3.30 \times 10^2 \times (10^{-3} \text{ kg}) \text{ (since } 1 \text{ g} = 10^{-3} \text{ kg)}$$

$$= 0.330 \text{ kg}$$

- (ii) Similarly, for the first entry in the second column:

$$V/10^2 \text{ cm}^3 = 2.00$$

$$\text{So } V = 2.00 \times 10^2 \text{ cm}^3$$

$$= 2.00 \times 10^2 \times (10^{-2} \text{ m})^3 \text{ (since } 1 \text{ cm} = 10^{-2} \text{ m)}$$

$$= 2.00 \times 10^2 \times 10^{-6} \text{ m}^3$$

$$= 2.00 \times 10^{-4} \text{ m}^3$$

- (b) The plot is shown in Figure A5. (Note that the volume is plotted along the horizontal (x) axis because it is the independent variable (the volume of liquid can be varied at will); the dependent variable, the mass, is plotted along the vertical (y) axis. Note also that the axes are labelled in just the same way as the columns of data in Table 3.)

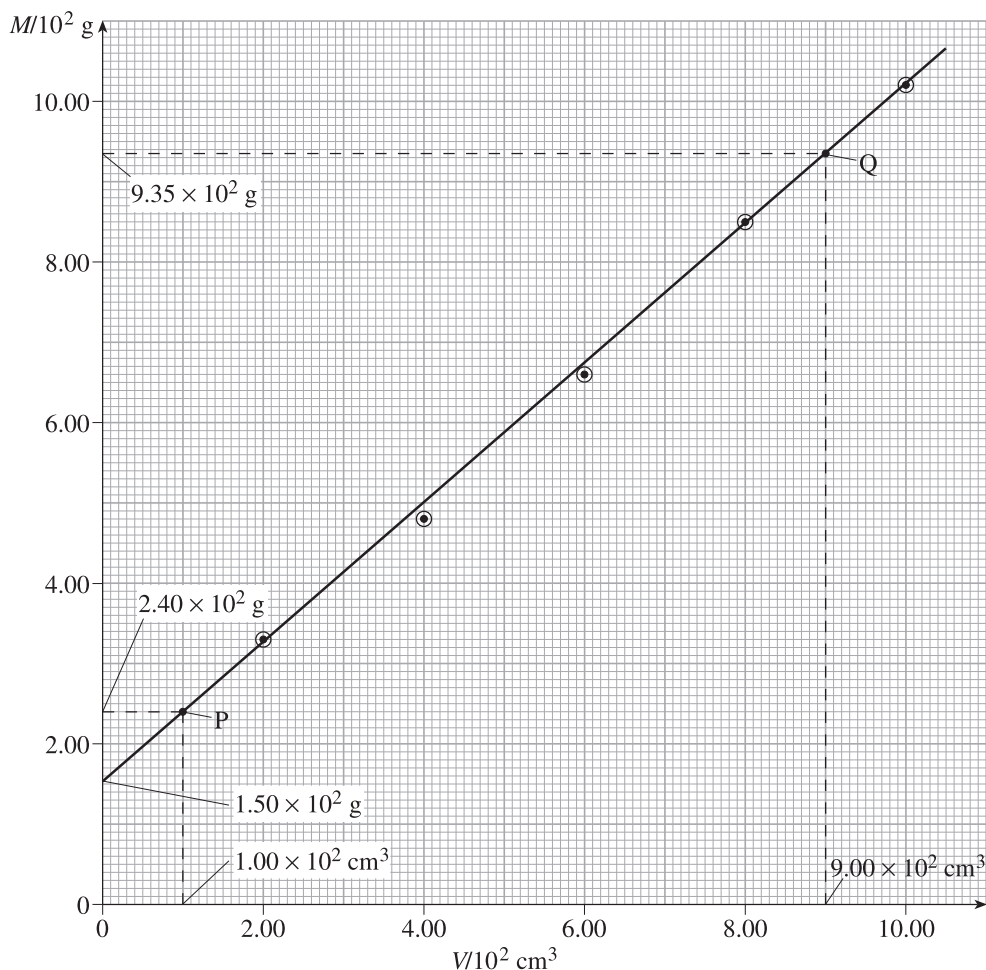


Figure A5 Plot of the mass, M , of a flask against the volume, V , of the liquid it contains, using the data in Table 3.

The standard equation for a straight-line plot is $y = mx + c$, where m is the slope and c is the intercept on the y -axis (when $x = 0$). In this case, x is the volume V of liquid, and y is the mass M of the flask + liquid; so the intercept on the y -axis is just the mass of the empty flask (i.e. $c = M_0$). So you can write:

$$M = M_0 + \rho V$$

where the slope of the graph (now given the symbol ρ) is actually the density of the liquid. Using the two points indicated in Figure 2 (including units and powers of ten):

$$\rho = \frac{(9.35 - 2.40) \times 10^2 \text{ g}}{(9.00 - 1.00) \times 10^2 \text{ cm}^3} = 0.87 \text{ g cm}^{-3}$$

$$M_0 = 1.50 \times 10^2 \text{ g} = 150 \text{ g}$$

Question 4.4

In general, it is best to choose points on the straight lines that are well separated. And don't forget to include the *units* of the quantities involved, as indicated by the labels on the axes (which may involve powers of ten as well; see Question 4.3). Sample calculations are as follows:

$$(a) \text{ slope} = \frac{8 \text{ m} - 0 \text{ m}}{15 \text{ s} - 0 \text{ s}} = 0.53 \text{ m s}^{-1}$$

$$(b) \text{ slope} = \frac{294 \text{ K} - 300 \text{ K}}{30 \text{ s} - 5 \text{ s}} = -0.24 \text{ K s}^{-1}$$

Notice that here the slope is *negative*, as would be expected since the temperature decreases with increasing time.

7 Suggested further reading/revision

Other than the module materials for S215, S104 and S141, the following books and eBooks may provide useful revision before S315.

- The Open University books from the Level 2 module S205 *The Molecular World* were co-published with the RSC and are available separately, and as eBooks from the Library.

A good general chemistry book is provided by:

- A Burrows, J Holman, A Parsons, G Pilling and G Price, *Chemistry³: Introducing inorganic, organic and physical chemistry* (2nd edition, 2013), Oxford University Press. This comprehensive textbook covers the introductory material normally introduced in the first year of chemistry courses at UK universities. It provides breadth of coverage of the whole of chemistry and with depth of information on individual topics.

The following books cover more specialised areas of chemistry in physical, organic and inorganic chemistry. They may be useful for revision of S215 and also in your study of S315.

- P. W. Atkins, L. Jones and L Laverman *Chemical Principles: The Quest For Insight* (6th edition, 2013), W H Freeman.
- P. W. Atkins and J. de Paula, *Elements of Physical Chemistry* (6th edition, 2012), Oxford University Press.
- J McMurry, *Organic Chemistry* (8th edition, 2011), Brooks/Cole.
- J Clayden, N Greeves and S Warren, *Organic Chemistry* (2012) Oxford University Press. A classic organic chemistry text with very careful explanations of difficult concepts and examples related to everyday life.
- P Atkins, T Overton, J Rourke, *Shriver and Atkins' Inorganic Chemistry* (2009) Oxford University Press.

In addition, the following books cover the mathematical concepts required for S315 (and more).

- Northedge, J. Thomas, A. Lane and A. Peasgood, *The Sciences Good Study Guide* (1997) The Open University. Contains *Maths Help*, and covers basic mathematical skills in a readable and user-friendly style.
- P Yates, *Chemical Calculations at a Glance* (2005) Wiley-Blackwell. This book shows how maths is applied in chemistry and includes problems (with answers). This book is available as an eBook from the OU Library.

8 Appendix

The Appendix contains the following S215 *Data Book* tables and data:

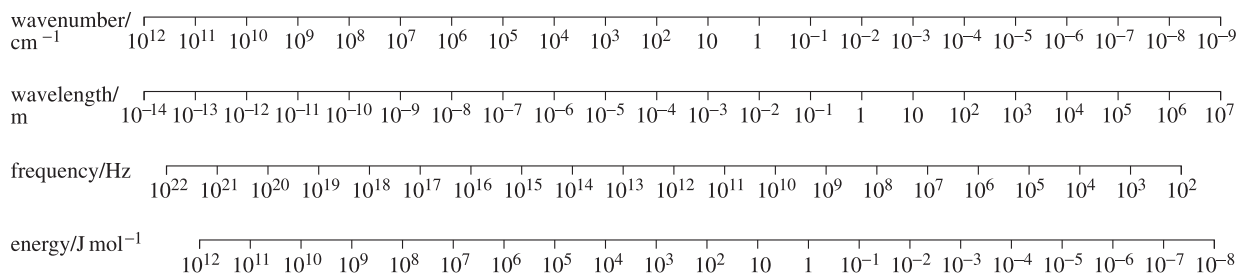
- Order of priority
- The electromagnetic spectrum and unit conversion scales
- The infrared correlation chart and Infrared absorption wavenumbers
- The ¹³C NMR correlation chart
- Functional group interconversions table

Order of priority

Order of priority of atoms and groups for application of the sequence rules.

HIGHEST PRIORITY		
-I	-CH=CHCOOH	-C ₆ H ₁₁ (cyclohexyl)
-Br	-C(CH ₃) ₃	-CH=CHCH ₃
-Cl	-C≡CH	-CH=CH ₂
-SO ₃ H	-C ₆ H ₅	-CH(CH ₃) ₂
-SO ₂ CH ₃	-CH ₂ NH ₂	-CH ₂ COCH ₃
-SOCH ₃	-C≡N	-CH ₂ CHO
-SCH ₃	-CH ₂ OH	-CH ₂ C ₆ H ₅
-SH	-CHO	-CH ₂ C≡CH
-F	-COCH ₃	-CH ₂ CH=CH ₂
-OCOCH ₃	-CONH ₂	-CH ₂ CH(CH ₃) ₂
-OC ₆ H ₅	-COOH	-CH ₂ CH ₂ CH(CH ₃) ₂
-OCH ₂ C ₆ H ₅	-COOCH ₃	-CH ₂ CH ₂ CH ₂ CH ₂ CH ₃
-OCH ₃	-CH ₂ SH	-CH ₂ CH ₂ CH ₂ CH ₃
-OH	-CH ₂ Cl	-CH ₂ CH ₂ CH ₃
-NO ₂	-COCl	-CH ₂ CH ₃
-NO	-NH ₂	-CH ₃
-NHCOCH ₃	-NH ₃ ⁺	-H
-N(CH ₃) ₂	-NHCH ₃	non-bonded pair of electrons
		LOWEST PRIORITY

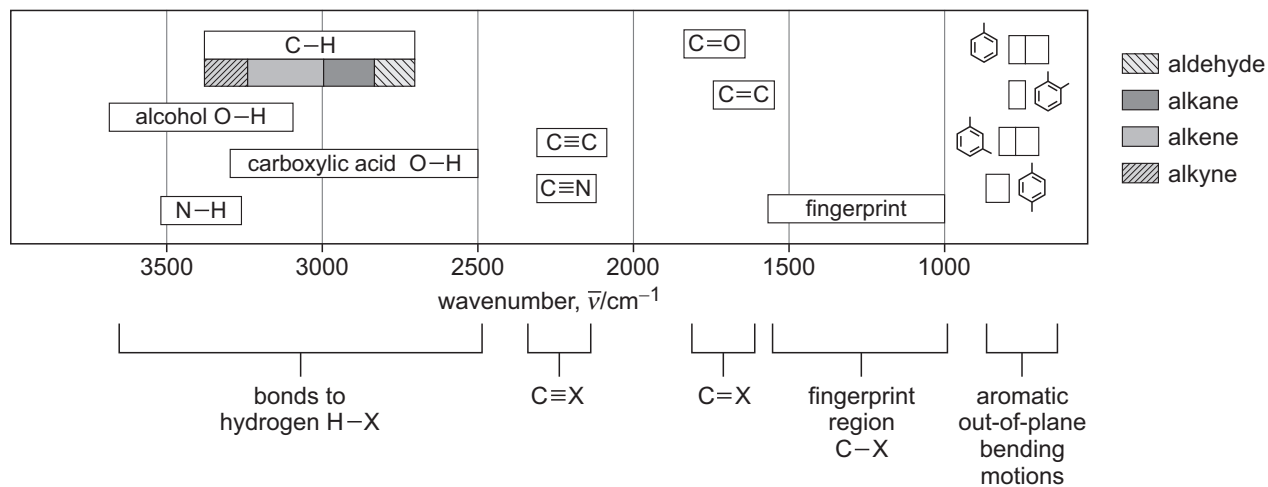
The electromagnetic spectrum and unit conversion scales



RADIATION CLASSIFICATION

γ -rays	
X-rays	
ultraviolet	
visible	
infrared	
microwave	
radiowave	
audio	

The infrared correlation chart



The infrared correlation chart.

Infrared absorption wavenumbers

Infrared absorption wavenumbers of C–H groups

Characteristic infrared absorption wavenumbers of C–H groups

C–H group	Wavenumber range/cm ⁻¹
saturated aliphatic, $\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	just below 3 000
unsaturated, C=C–H	just above 3 000
alkyne, C≡C–H	3 250–3 310
aldehyde, $\begin{array}{c} \text{C}-\text{C}-\text{H} \\ \\ \text{O} \end{array}$	2 710–2 730

Infrared absorption wavenumbers of aromatic compounds

Characteristic infrared absorption wavenumbers of aromatic compounds

Group	Wavenumber range/cm ⁻¹
aromatic C–H stretch	3 010–3 040 (medium intensity)
aromatic ring vibrations	≈ 1 600 (medium intensity) ≈ 1 580 (variable intensity) ≈ 1 500 (medium intensity)

Infrared absorption wavenumbers of C=O absorptions in different types of carbonyl compound

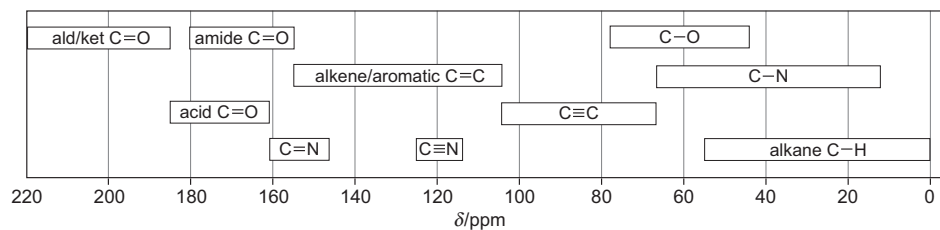
Characteristic infrared absorption wavenumbers of C=O absorptions in different types of carbonyl compound (asterisks * indicate that conjugation with a double bond or an aromatic ring lowers the wavenumber of these absorptions by 10–20 cm⁻¹, and daggers † by 25–40 cm⁻¹)

Class of compound	Wavenumber range/cm ⁻¹
amide	1 650–1 690
acid*	1 700–1 725
ketone†	1 705–1 725
aldehyde†	1 720–1 740
ester*	1 735–1 750
anhydride*	two absorptions near 1 770 and 1 830
acid chloride*	1 785–1 815

The ^{13}C NMR correlation chart

The following figure shows the range, in terms of δ values, over which a particular group is expected to yield a peak in the ^{13}C NMR spectrum.

The compounds in this figure are restricted to those containing carbon, hydrogen, oxygen and nitrogen.



The ^{13}C NMR correlation chart (relative to TMS = 0 ppm).

Table 2.1 Functional group interconversions.

Functional group in starting material \ Functional group in product	C-OH	C-NH ₂	C-Cl (or C-Br)	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{C} \end{array}$	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{H} \end{array}$	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{HO} \end{array}$	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{RO} \end{array}$	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{RHN} \end{array}$	$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{Cl} \end{array}$	C≡N	C=C	C≡C	$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$
C-OH	•	⑨	⑭	⑳	⑳	㉓	㉓	—	㉓	—	⑳⑥	—	—
C-NH ₂	—	•	—	—	—	—	—	㉑	—	⑳④	—	—	—
C-Cl (or C-Br)	①	⑩	•	—	—	—	—	—	—	—	⑳⑦	⑳⑩	⑳②
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{C} \end{array}$	②	—	—	•	—	—	—	—	—	—	⑳⑧	—	—
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{H} \end{array}$	③	—	—	—	•	—	—	—	—	—	—	—	—
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{HO} \end{array}$	④	⑪	⑮	—	㉒	•	㉑	⑳⑩	⑳①	⑳⑤	⑳⑨	—	—
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{RO} \end{array}$	⑤	—	—	—	—	⑳④	•	—	⑳②	—	—	—	—
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{RHN} \end{array}$	—	⑫	—	—	—	⑳⑤	⑳⑧	•	⑳③	—	—	—	—
$\begin{array}{c} \text{C} \\ \diagdown \quad \diagup \\ \text{C}=\text{O} \\ \text{Cl} \end{array}$	—	—	—	—	—	⑳⑥	—	—	•	—	—	—	—
C≡N	⑥	⑬	⑯	—	—	—	—	—	—	•	—	—	—
C=C	⑦	—	⑰	—	—	—	—	—	—	—	•	⑳①	—
C≡C	—	—	⑱	—	—	—	—	—	—	—	—	•	—
$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array}$	⑧	—	⑲	㉑	㉑	—	—	—	—	—	—	—	•

Table entry no.	Reaction
1	$\text{ROH} \xrightarrow[\text{(or HBr)}]{\text{HCl}} \text{RCl (or RBr)}$ $\text{ROH} \xrightarrow{\text{SOCl}_2} \text{RCl}$
2	$\begin{array}{c} \text{R}^1 \\ \\ \text{CH-OH} \\ \\ \text{R}^2 \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \begin{array}{c} \text{R}^1 \\ \\ \text{C=O} \\ \\ \text{R}^2 \end{array}$ $\begin{array}{c} \text{R}^1 \\ \\ \text{CH-OH} \\ \\ \text{R}^2 \end{array} \xrightarrow[\text{or CrO}_3/\text{H}_2\text{SO}_4/\text{propanone}]{\text{CrO}_3/\text{pyridine} \text{ or } \text{CrO}_3/\text{pyridine}/\text{HCl (PCC)}} \begin{array}{c} \text{R}^1 \\ \\ \text{C=O} \\ \\ \text{R}^2 \end{array}$
3	$\text{RCH}_2\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7 \text{ (or } \text{Na}_2\text{Cr}_2\text{O}_7)} \text{RCHO}$ <p>(care needs to be exercised so as to avoid further oxidation of the aldehyde product to the corresponding carboxylic acid; see entries 4 and 22)</p> $\text{RCH}_2\text{OH} \xrightarrow[\text{or CrO}_3/\text{pyridine}/\text{HCl}]{\text{CrO}_3/\text{pyridine}} \text{RCHO}$ $\text{RCH}_2\text{OH} \xrightarrow{\text{MnO}_2} \text{RCHO}$
4	$\text{RCH}_2\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7 \text{ (or } \text{Na}_2\text{Cr}_2\text{O}_7)} \text{RCOOH}$ $\text{RCH}_2\text{OH} \xrightarrow[\text{low temp.}]{\text{CrO}_3/\text{H}_2\text{SO}_4/\text{propanone}} \text{RCOOH}$
5	$\text{R}^1\text{OH} \xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{R}^2\text{COOH}} \begin{array}{c} \text{O} \\ \\ \text{R}^1\text{O}-\text{C}-\text{R}^2 \end{array}$ $\text{R}^1\text{OH} \xrightarrow{\begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{R}^2-\text{C}-\text{O}-\text{C}-\text{R}^2 \end{array}} \begin{array}{c} \text{O} \\ \\ \text{R}^1\text{O}-\text{C}-\text{R}^2 \end{array}$ $\text{R}^1\text{OH} \xrightarrow{\begin{array}{c} \text{O} \\ \\ \text{R}^2-\text{C}-\text{Cl} \end{array}} \begin{array}{c} \text{O} \\ \\ \text{R}^1\text{O}-\text{C}-\text{R}^2 \end{array}$
6	$\text{R}^1\text{OH} \xrightarrow{\text{TsCl}} \text{ROTs} \xrightarrow{\text{KCN}} \text{R}-\text{C}\equiv\text{N}$ <p>(TsCl = <i>para</i>-toluenesulfonyl chloride, or tosyl chloride)</p>
7	$\text{RCH}_2\text{CH}_2\text{OH} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{R}-\text{CH}=\text{CH}_2$
8	$\text{R-OH} \xrightarrow[\text{(ii) Bu}^t_3\text{SnH/AIBN}]{\text{(i) Cl}-\begin{array}{c} \text{S} \\ \\ \text{C}-\text{R}^1 \end{array}} \text{R-H}$ <p>Bu^t = (CH₃)₃C- AIBN = αα'-azo-bis-isobutyronitrile</p>

Table entry no.	Reaction
9	$\text{ArNH}_2 \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) HCl/NaNO}_2/0^\circ\text{C}} \text{ArOH}$ <p>(only for aromatic primary amines; that is, where Ar is an aryl group)</p>
10	$\text{ArNH}_2 \xrightarrow[\text{(ii) CuCl}]{\text{(i) HCl/NaNO}_2/0^\circ\text{C}} \text{ArCl}$ <p>(only for aromatic primary amines; that is, where Ar is an aryl group)</p>
11	$\text{ArNH}_2 \xrightarrow[\text{(iii) H}^+/\text{H}_2\text{O}]{\text{(i) HCl/NaNO}_2/0^\circ\text{C}, \text{(ii) CuCN}} \text{ArCOOH}$ <p>(only for aromatic primary amines; that is, where Ar is an aryl group)</p>
12	$\text{R}^1\text{NH}_2 \xrightarrow[\text{(ii) } >200^\circ\text{C}]{\text{(i) R}^2\text{CO}_2\text{H}} \text{R}^1\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$ $\text{R}^1\text{NH}_2 \xrightarrow{\text{R}^2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}^3} \text{R}^1\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$ $\text{R}^1\text{NH}_2 \xrightarrow{\text{R}^2-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}} \text{R}^1\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$ $\text{R}^1\text{NH}_2 \xrightarrow{\text{R}^2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2} \text{R}^1\text{HN}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}^2$
13	$\text{ArNH}_2 \xrightarrow[\text{(ii) CuCN}]{\text{(i) HCl/NaNO}_2/0^\circ\text{C}} \text{Ar}-\text{C}\equiv\text{N}$ <p>(only for aromatic primary amines; that is, where Ar is an aryl group)</p>
14	$\text{RCl (or Br)} \xrightarrow{\text{H}_2\text{O}/\text{HO}^-} \text{ROH}$
15	$\text{RCl} \xrightarrow[\text{(iii) H}^+/\text{H}_2\text{O}]{\text{(i) Mg/ether}, \text{(ii) CO}_2} \text{RCOOH}$
16	$\text{RBr} \xrightarrow{\text{NaCN}} \text{R}-\text{C}\equiv\text{N}$
17	$\text{RCH}_2\text{CH}_2\text{Cl (or Br)} \xrightarrow{\text{NaOBu}^t} \text{R}-\text{CH}=\text{CH}_2$ <p>(elimination competes with substitution, and is preferred if a sterically hindered base like NaOBu^t is used) Bu^t = (CH₃)₃C-</p> $\text{R}-\underset{\text{Br}}{\text{C}}-\text{CH}_2\text{Br} \xrightarrow[\text{or I}^-]{\text{Zn}} \text{R}-\text{CH}=\text{CH}_2$ <p>(only for 1,2-disubstituted bromoalkanes)</p>

Table entry no.	Reaction
18	$\text{RCH}_2\text{CHCl}_2 \xrightarrow{\text{NaNH}_2} \text{R}-\text{C}\equiv\text{C}-\text{H}$ $\text{RCHClCH}_2\text{Cl} \xrightarrow{\text{NaNH}_2} \text{R}-\text{C}\equiv\text{C}-\text{H}$
19	$\text{R}-\text{Br} \xrightarrow[\text{AIBN}]{\text{Bu}_3\text{SnH}} \text{R}-\text{H} \quad \text{Bu} = \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$
20	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2 \end{array} \xrightarrow[\text{(ii) H}^+/\text{H}_2\text{O}]{\text{(i) LiAlH}_4 \text{ or NaBH}_4} \text{R}^1\text{R}^2\text{CHOH}$ <p>(for aldehydes and ketones; aldehydes react faster than ketones, and LiAlH₄ is more reactive than NaBH₄)</p>
21	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2 \end{array} \xrightarrow{\text{Zn/HCl}} \text{R}^1-\text{CH}_2-\text{R}^2$ $\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2 \end{array} \xrightarrow[\text{(ii) 200}^\circ\text{C}]{\text{(i) H}_2\text{NNH}_2} \text{R}^1-\text{CH}_2-\text{R}^2$
22	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H} \end{array} \xrightarrow[\text{H}_2\text{SO}_4]{\text{K}_2\text{Cr}_2\text{O}_7} \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$
23	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{X} \end{array} \xrightarrow[\text{(ii) H}^+/\text{H}_2\text{O}]{\text{(i) LiAlH}_4} \text{RCH}_2\text{OH}$ <p>(X = OH, OR, OCOR, Cl)</p>
24	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array} \xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{R}^2\text{OH}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{O} \end{array}$ $\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{O}^- \end{array} \xrightarrow{\text{R}^2\text{Br}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{O} \end{array}$
25	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array} \xrightarrow[\text{(ii) heat, >200}^\circ\text{C}]{\text{(i) R}^2\text{NH}_2} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{HN} \end{array}$
26	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array} \xrightarrow[\text{or SOCl}_2]{\text{PCl}_5} \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{Cl} \end{array}$

Table entry no.	Reaction
27	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{O} \end{array} \xrightarrow[\text{or HO}^-/\text{H}_2\text{O}]{\text{either H}^+/\text{H}_2\text{O}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array} + \text{R}^2\text{OH}$
28	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{O} \end{array} \xrightarrow{\text{R}^3\text{NH}_2} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^3\text{HN} \end{array} + \text{R}^2\text{OH}$
29	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{H}_2\text{N} \end{array} \xrightarrow{\text{LiAlH}_4} \text{RCH}_2\text{NH}_2$
30	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{HN} \end{array} \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array} + \text{R}^2\text{NH}_3^+$
31	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{Cl} \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{HO} \end{array}$
32	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{Cl} \end{array} \xrightarrow{\text{R}^2\text{OH}} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{O} \end{array}$
33	$\begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{Cl} \end{array} \xrightarrow{\text{R}^2\text{NH}_2} \begin{array}{c} \text{R}^1 \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}^2\text{HN} \end{array}$
34	$\text{R}-\text{C}\equiv\text{N} + 2\text{H}_2 \xrightarrow[\text{e.g. Pd}]{\text{catalyst}} \text{RCH}_2\text{NH}_2$
35	$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{or H}_2\text{O}/\text{NaOH}]{\text{either H}_2\text{O}/\text{H}_2\text{SO}_4} \text{RCOOH}$
36	$\text{R}-\text{CH}=\text{CH}_2 \xrightarrow{\text{H}^+/\text{H}_2\text{O}} \begin{array}{c} \text{R}-\text{CH}-\text{CH}_3 \\ \\ \text{OH} \end{array}$ <p>(this is the Markovnikov product)</p> $\text{R}-\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) H}_2\text{O}_2/\text{NaOH}]{\text{(i) 'BH}_3\text{'}} \text{RCH}_2\text{CH}_2\text{OH}$ <p>(this is the anti-Markovnikov product)</p>

Table entry no.	Reaction
37	$\text{R}-\text{CH}=\text{CH}_2 + \text{HX} \longrightarrow \text{R}-\underset{\text{X}}{\text{CH}}-\text{CH}_3$ <p style="text-align: center;">(X = Cl, Br, I)</p> $\text{R}-\text{CH}=\text{CH}_2 + \text{Br}_2 \longrightarrow \text{R}-\underset{\text{Br}}{\text{CH}}-\underset{\text{Br}}{\text{CH}_2}$
38	$\begin{array}{ccc} \text{R}^1 & & \text{R}^3 \\ & \backslash & / \\ & \text{C}=\text{C} & \\ & / & \backslash \\ \text{R}^2 & & \text{R}^4 \end{array} \xrightarrow{\text{KMnO}_4/\text{H}^+} \begin{array}{c} \text{R}^1 \\ \\ \text{C}=\text{O} \\ \\ \text{R}^2 \end{array} + \begin{array}{c} \text{R}^3 \\ \\ \text{C}=\text{O} \\ \\ \text{R}^4 \end{array}$
39	$\text{R}^1-\text{CH}=\text{CH}-\text{R}^2 \xrightarrow{\text{KMnO}_4/\text{H}^+} \text{R}^1\text{COOH} + \text{R}^2\text{COOH}$
40	$\text{R}-\text{C}\equiv\text{C}-\text{H} + 2\text{HBr} \longrightarrow \text{RCBr}_2\text{CH}_3$
41	$\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2 \xrightarrow[\text{catalyst}]{\text{H}_2/\text{Lindlar's}} \begin{array}{ccc} \text{R}^1 & & \text{R}^2 \\ & \backslash & / \\ & \text{C}=\text{C} & \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$ <p style="text-align: center;">(the product has <i>Z</i> stereochemistry)</p> $\text{R}^1-\text{C}\equiv\text{C}-\text{R}^2 \xrightarrow[\text{liquid NH}_3]{\text{Na}} \begin{array}{ccc} \text{R}^1 & & \text{H} \\ & \backslash & / \\ & \text{C}=\text{C} & \\ & / & \backslash \\ \text{H} & & \text{R}^2 \end{array}$ <p style="text-align: center;">(the product has <i>E</i> stereochemistry)</p>
42	$\begin{array}{c} \\ -\text{C}-\text{H} \\ \end{array} \xrightarrow[h\nu]{\text{Br}_2} \begin{array}{c} \\ -\text{C}-\text{Br} \\ \end{array}$ <p style="text-align: center;">(not always very selective!)</p>