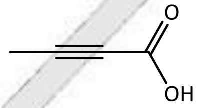
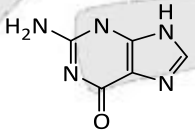
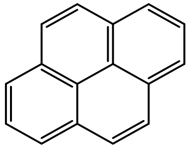
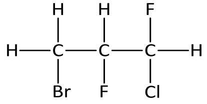
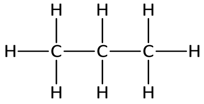
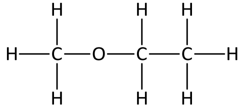
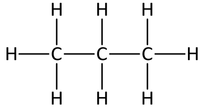
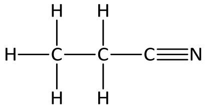
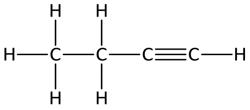
11.1

Index of hydrogen deficiency (IHD) for determining unsaturation

The index of hydrogen deficiency (IHD) is the number of C=C double bonds (or equivalent) in an organic molecule, with the term "double bond or equivalent" encompassing a double bond or a ring. A triple bond can be treated as two double bond equivalents.

For molecules whose structural formula is known, math AISL students tend to mindlessly use the formula, when in fact they could have figured out IHD value simply by counting the total number of double bonds or rings within the structural formula. For example, benzene has an IHD of 4, because a benzene ring possesses 3 double bonds as well as the ring structure which represents another unsaturation. IHD, however, is more often used for problem solving involving organic compounds with known molecular formula but unknown structural formula. A mathematical formula that can help you calculate the IHD of a molecular formula is IHD $= \frac{2C+2-H}{2}$. Heteroatoms (atoms other than carbon and hydrogen) require special treatments, according the table below

Example structures	IHD
	A double bond and a triple represent a total of 1 + 2 = 3 unsaturations, hence the IHD of this molecule is 3.
	The molecule has 2 rings + 4 double bonds, hence its IHD value is 6.
	This molecule has 4 rings and 8 double bonds for an IHD value of 4 + 8 = 12.

Heteroatom	Treatment	Reason	Example
Halogens	Treat as H	Halogen atoms, much like the hydrogen atom, form exactly 1 bond within typical organic compounds.	 $C_3H_4F_2BrCl$  C_3H_8
Oxygen	Ignore	Introduction or removal of oxygen atoms does not create or require bonding openings with an organic structural formula.	 C_3H_8O  C_3H_8
Nitrogen	Treat as 1 C + 1 H	On paper, a nitrogen atom can replace a CH within an organic molecule without creating or requiring bonding openings.	 C_3H_5N  C_4H_6

As the IHD formula is obscure and not provided, Akademia experts suggest that for solving problems that involve the determination of IHD from a molecular formula, the index of hydrogen deficiency should be interpreted as the number of "unsaturations" (double bonds or equivalent) that can be formed, **as a result of hydrogen atoms being removed from a fully saturated molecule.** We strongly recommend the following approach instead: **determine the number of "unsaturations" on a molecule by comparing its molecular formula to the formula of a fully saturated molecule of the same number of carbon atoms – basically C_nH_{2n+2}, and recognise that one unsaturation is created for every two hydrogens removed.**

Example 1. The molecule $C_9H_8O_4$ is 12 hydrogens short of the fully saturated C_9 molecule – C_9H_{20} according the alkane general formula C_nH_{2n+2}. As a result, the molecule $C_9H_8O_4$ must contain $\frac{12}{2} = 6$ unsaturations.
Example 2. The molecule $C_3H_5NO_2$ is equivalent to C_4H_6, which is 4 hydrogens short of the C_4 alkane of C_4H_{10}. Hence $C_3H_5NO_2$ has 2 unsaturations.

Students should keenly use IHD values in organic chemistry problem solving. Specifically, when deducing the structure of an unknown compound from spectroscopic data or reactivity information, students should rule out impossible structures or functional groups (e.g. $C_4H_{10}O$ cannot be a ketone because its IHD is 0 and cannot explain the presence of the ketone C=O) that are inconsistent with IHD information.

11.1

Significant figure determination

Some rules for determining the number significant figures in numbers that contain leading and/or trailing zeroes are as follows:

Type of number	Rule	Number, and number of significant figures	
Value smaller than 1	The leading zeros are all non–significant, and the in–between and trailing zeros are all significant.	0.000$\underline{20}$ 0.0$\underline{305000}$	2 6
Number value larger than 1 with no decimals	The in–between zeros are all significant. The trailing zeros may or may not be significant – this depends on the precision level, which may be expressed in words or using metric multipliers.	$\underline{207}$0 correct to the nearest ten $\underline{2070}$ correct to the nearest integer	3 4
Number value larger than 1 with decimals	All in–between zeros and trailing zeros are significant.	$\underline{24.80}$ $\underline{6.0200}$	4 5
Exact count	An exact count has no uncertainties and has an infinite number of significant figures.	$\underline{10}$ math AISL students $\underline{140}$ test–tubes $\underline{14}$0 test–tubes correct to the nearest 10	infinite infinite 2
Standard form number	The number of significant figures of a standard–form number is the number of significant figures in the front number (formally called the mantissa)	$\underline{1.7} \times 10^{-8}$ $\underline{5.680} \times 10^{2}$	2 4

11.1	Absolute uncertainty, fractional uncertainty, percentage uncertainty	The absolute uncertainty of a measured quantity depends on the precision of the instrument. • For a single measurement taken from a digital instrument, the absolute uncertainty is the smallest displayable value. For example, a reading of 1.80 grams from a digital balance that measures correct to 2 decimal places will have an absolute uncertainty of ± 0.01 g. • For a single measurement taken from an analogue instrument, the absolute uncertainty is half the smallest scale division. For example, the absolute uncertainty of a single burette reading of 10.40 cm^3 is ± 0.05 cm^3. • Volumetric glasswares, such as volumetric flasks and volumetric pipettes, are "you have one job" –type glasswares, and are manufactured in a way so that the absolute uncertainty is specified on the glassware. For example, a volumetric flask is typically manufactured to allow the preparation of a 250.0 ± 0.3 cm^3 of a solution. • For a set of measurements, the absolute uncertainty is taken to be the half–range of the data set if the half–range exceeds the instrumental uncertainty. For example, a set of volumes of 15.20 cm^3, 15.40 cm^3 and 15.60 cm^3 has an absolute uncertainty of $\frac{15.60-15.20}{2} = 0.20\ \text{cm}^3$. Fractional uncertainty (sometimes called relative uncertainty) $= \frac{\text{absolute uncertainty}}{\text{value}}$. For example, the fractional uncertainty of a reading of 1.80 ± 0.01 g is $\frac{0.01}{1.80} = 0.0056$. It is important to note that fractional uncertainties should not be presented as fractions on an exam. Percentage uncertainty $= \frac{\text{absolute uncertainty}}{\text{value}} \times 100\%$. For example, the percentage uncertainty associated with the measurement of 1.80 ± 0.01 g is $0.0056 \times 100\% = 0.56\%$
11.1	Accuracy, systematic error	Accuracy refers to how close a measurement or an experimental result is to the true value / literature value / commonly accepted value. A systematic error is an error that results in all measurements deviating from the true value by the same amount. Systematic errors usually lead to low accuracy. A measurement or an experiment is accurate if the commonly accepted value is within the experimental error range. For example, an experiment in determining the water of crystallisation of $CuSO_4 \bullet xH_2O$ results in $x = 4.88 \pm 0.19$. The established value is $x = 5$. Since 5 is within 4.88 ± 0.19, this experimental result can be deemed accurate. Accuracy can also be determined via calculating the experimental error. For example, an ethanol combustion experiment yields a ΔH value of –1038 ± 20 kJ mol^{-1}, while the true (literature) value is –1367 kJ mol^{-1}. The percentage experimental error incurred $= \left\lvert \frac{1038-1367}{1367} \right\rvert \times 100\% = 24.1\%$, which is bigger than the experimental random uncertainty of $\frac{20}{1038} = 1.9\%$. This indicates that the experiment is inaccurate, and significant systematic error has been incurred. Systematic errors can be…… • due to a mis–calibrated measuring instrument e.g. thermometer, pH meter; • due to poor experimental design e.g. not cooling a wire prior to measuring currents during an electrolysis experiment; • due to poor measuring technique e.g. parallax error while reading the volume of liquid in a measuring cylinder, not zeroing a balance prior to measuring mass; • inevitable e.g. thermal energy loss to the surroundings.
11.1	Precision, random error, rounding	Precision can refer to…… • the number of significant figures for a single measurement, or • how close a set of measurements is compared to each other, or • the standard deviation for a set of measurements. A single measurement is precise if it has a small relative or percentage uncertainty. For example, a single balance reading of 2.50 grams has a percentage uncertainty of $\frac{0.01}{2.50} = 0.4\%$. In quantitative analytic chemistry, a percentage uncertainty of less than 1% is often deemed precise. Meanwhile, a set of measurement is precise if it has a small range (or small standard deviation – used more frequently in biology). For example, a set of volumes of 15.50 cm^3, 15.40 cm^3 and 15.60 cm^3 is precise, because the mean value of 15.50 cm^3 has an absolute uncertainty of $\frac{15.60-15.40}{2} = 0.10\ \text{cm}^3$. The associated percentage uncertainty is $\frac{0.10}{15.50} = 0.65\%$ which is a small value – this allows the set of volume data to be deemed precise. Random errors are random deviation from the true values. Random errors incurred during a single measurement are often due to imprecise equipments, while experimental random errors are often due to skill issues of the person who conducted the experiment. Random errors usually lead to low precision. Random errors can be reduced by using more precise measuring instruments, or by taking repeated readings.
11.1	Rounding	When adding and subtracting quantities with uncertainties, the final value is rounded according to the least precise number in terms of decimal places. For example, $12.38\ \text{g} + 2.9\ \text{g} = 15.28\ \text{g}$ which should be rounded to 15.3 g, as the least precise figure of 2.9 g has 1 decimal place. When multiplying and dividing quantities with uncertainties, the final value is rounded according to the least precise number in terms of significant figures. For example, $0.028\ \text{mol} \times 44.01\ \text{g mol}^{-1} = 1.23228\ \text{g}$ which should be rounded to 1.2 g, as the least precise figure of 0.028 mol contains 2 significant figures.

11.1

Uncertainty propagation

When adding and subtracting quantities with uncertainties, the absolute uncertainties are added.

Worked example. During a titration, the burette readings for the volume of HCl before and after are 2.50 and 18.75 cm^3, respectively. Both readings are associated with an absolute uncertainty of 0.05 cm^3. Determine the volume of HCl added, including its absolute uncertainty.
Suggested answer: The volume added = 18.75 – 2.50 = 16.25 cm^3 and the absolute uncertainty of the final volume, ΔV, is 0.05 + 0.05 = 0.10 cm^3.

When multiplying and dividing quantities with uncertainties, the fractional or percentage uncertainties are added, and the absolute uncertainty equals to the final fractional or percentage uncertainty multiplied by the final quantity itself.

Worked example. An average of 16.25 ± 0.10 cm^3 of HCl is needed to neutralise 25.00 ± 0.03 cm^3 of 0.178 ± 0.001 mol dm^{-3} Na_2CO_3. Determine the concentration of the HCl used, including its absolute uncertainty.
Suggested answer: The balanced equation for the reaction is $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$. We can use the equation $\frac{C_AV_A}{C_BV_B} = \frac{n_A}{n_B}$ to first determine the concentration of HCl to be $C_A = \frac{n_A}{n_B} \times \frac{C_BV_B}{V_A} = \frac{2}{1} \times \frac{(0.178)(0.02500)}{(0.01625)} = 0.548 \text{ mol dm}^{-3}$.
To calculate the absolute uncertainty in the concentration of HCl (ΔC_A), we first calculate the final percentage uncertainty, which is the sum of the percentage uncertainties of the values used.
Note that the equation coefficients have no uncertainties, hence the final percentage uncertainty of the concentration of HCl
$= \%$ uncertainty in $C_B + \%$ uncertainty in $V_B + \%$ uncertainty in V_A
$= \left(\frac{0.001}{0.178} + \frac{0.03}{25.00} + \frac{0.10}{16.25}\right) \times 100\% = 1.30\%$
Now the absolute uncertainty can be calculated by multiplying the final value by the final percentage uncertainty:
$\frac{\Delta C_A}{C_A} = 1.30\%, \Delta C_A = 1.30\% \times C_A = 1.30\% \times 0.548 = 7.10 \times 10^{-3} \text{mol dm}^{-3}$
Using rounding rules allows us to conclude that the concentration of HCl is 0.548 ± 0.007 mol dm^{-3}.

A more complicated example is as follows:

Worked example. In a calorimetry experiment, the following data is collected and used to calculate the value of ΔH for the combustion of ethanol. Determine the value of ΔH for the combustion of ethanol and its uncertainties.

Raw data	Suggested answers
Mass of water = 20.00 ± 0.01 grams Initial temperature = 25.0 ± 0.1°C Final temperature = 35.1 ± 0.1°C Specific heat capacity of water = 4.18 J g^{-1}°C^{-1} Mass of ethanol burnt = 0.164 ± 0.002 g Molar mass of ethanol = 46.08 g mol^{-1}	Using the formula $\Delta H = \frac{-mc\Delta T}{n}$, $\Delta H = \frac{-20.00 \times 4.18 \times (35.1-25.0)}{\left(\frac{0.164}{46.08}\right)} = -237244.5659 \ldots\ldots = -237 \text{ kJ mol}^{-1}$ Since ΔH is calculated mainly by multiplication and division, we next calculate the fractional (or percentage) uncertainty in ΔH: $\frac{\Delta(\Delta H)}{\Delta H} = \frac{\Delta m,H_2O}{m,H_2O} + \frac{\Delta(\Delta T)}{\Delta T} + \frac{\Delta m,\text{ethanol}}{m,\text{ethanol}}$ $= \frac{0.01}{20.00} + \frac{0.1 + 0.1}{10.1} + \frac{0.002}{0.164} = 0.0325$ (or 3.25%) The absolute uncertainty in ΔH $= 2.37 \times 10^5 \times 0.0325 = 7701 \ldots\ldots \text{ J mol}^{-1}$ Therefore the enthalpy of combustion of ethanol is determined from this experiment to be $-237 \pm 8 \text{ kJ mol}^{-1}$.

For rounding calculated quantities whose percentage uncertainties have been propagated, there are two common treatments:

Which assessment within the IB world?	Rule	Sample calculation
Paper 2 and 3	The final value is rounded according to the aforementioned rules, and the absolute uncertainty is rounded to the same level of <u>decimal place precision.</u>	<u>Worked example.</u> Calculate the speed when an object travels 1.2 ± 0.1 m in 1.4 ± 0.2 seconds. Suggested answer: Speed $= \frac{1.2}{1.4} = 0.85714 \ldots\ldots = 0.86 \text{ m s}^{-1}$ (2 s. f.) Fractional uncertainty $= \frac{1}{12} + \frac{2}{14} = 0.226 \ldots\ldots$ Absolute uncertainty $= 0.86 \times 0.226 = 0.193 \ldots\ldots$ Speed $= 0.86 \pm 0.19 \text{ m s}^{-1}$
Internal assessments	The absolute uncertainty is first calculated and rounded to 1 s. f., and the quantity itself is then rounded to the same level of <u>decimal place precision.</u>	<u>Worked example.</u> Calculate the speed when an object travels 1.2 ± 0.1 m in 1.4 ± 0.2 seconds. Suggested answer: Speed $= \frac{1.2}{1.4} = 0.85714 \ldots\ldots$ Fractional uncertainty $= \frac{1}{12} + \frac{2}{14} = 0.226 \ldots\ldots$ Absolute uncertainty $= 0.86 \times 0.226 = 0.193 \ldots\ldots = 0.2 \text{ m s}^{-1}$ (1 s. f.) Speed $= 0.9 \pm 0.2 \text{ m s}^{-1}$

11.2	Graphical analysis – practical graphs	Graphing is an important aspect of science. A suitable graph can help scientists determine unknown values and verify hypothetical mathematical relationships. The following table summarise the monitoring or summary graphs that students commonly encounter throughout the course.

Topic	Example	Independent variable	Possible dependent variables	Possible graphing and data processing
Ideal gas (Topic 1)	Boyle's law	Volume	Pressure	A plot of P vs. $\frac{1}{V}$ should be a straight line through the origin, with the value of the gradient corresponding to nRT.
	Avogadro's law	Mass of gas	Volume	Since $PV = \frac{mass}{M_r}RT$, a plot of V vs. m should be a straight line through the origin, with the value of the gradient corresponding to $\frac{RT}{PM_r}$.
	Charles' law	Kelvin temperature	Volume	A plot of V vs. T should be a straight line through the origin, with the value of the gradient corresponding to $\frac{nR}{P}$.
Calorimetry	Single–trial monitoring	Time	Temperature	The maximum theoretical temperature change can be deduced via extrapolation.
	Summary	Mass of fuel	Heat energy transferred	As $\Delta H = -\frac{Q}{(\frac{mass}{M_r})}$, a plot of Q vs mass should yield a straight line through origin, with the value of the gradient equaling to $-\frac{\Delta H}{M_r}$.
Thermometric titration (single–trial monitoring)		Volume of titrant	Temperature change	The maximum theoretical temperature and the end–point volume can be determined by extrapolating the warming and cooling sections.
Gibbs free energy analysis		Temperature	Gibbs free energy	The gradient corresponds to the negative of entropy of reaction (ΔS) while the y–intercept corresponds to the enthalpy of reaction (ΔH).
Kinetics – effect of concentration on reaction rate	Single–trial monitoring	Time	Volume of gas collected	Instantaneous reaction rates and average reaction rate can be determined by analyzing gradients. For HL students, the curvature can reveal the order of reaction with respect to a reactant.
	Summary	Concentration	Reaction rate (from processing the monitoring graphs), or relative rate $(\frac{1}{\text{time taken}})$ for observation to be made e.g. iodine clock turns permablack	(HL) A plot of reaction rate vs. concentration can reveal reaction orders and, with the value of the gradient possibly corresponding to rate constants.
Kinetics – effect of temperature on reaction rate	Single–trial monitoring	Time	Volume of gas collected	Instantaneous reaction rates and average reaction rates can be determined by analyzing gradients.
	Summary	Temperature	Reaction rate (from processing the monitoring graphs), or relative rate $(\frac{1}{\text{time taken}})$ for observation to be made e.g. iodine clock turns permablack	(HL) A plot of ln(rate) vs. $\frac{1}{T}$ has a gradient whose value equals to $-\frac{E_a}{R}$.
Acid–base titration (single–trial monitoring)		Volume of titrant	pH of reaction mixture	(HL) The equivalent–point volume can be determined. For a strong–weak titration, the pH of the half–equivalent point corresponds to the pK_a of the weak acid used.

<table>
<tr>
<td>11.2</td>
<td>Graphical analysis – proportion analysis</td>
<td>
The most commom examples of proportional relationship in chemistry involve direct proportion and inverse proportions. Non–proportional linear relationships also appear frequently within the syllabus.
<table>
<tr><th>Direct proportion</th><th>Inverse proportion</th><th>Linear, but not direct proportion</th></tr>
<tr>
<td>Straight line going through the origin.
Example: volume of a gas vs. Kelvin temperature</td>
<td>Curve with two asymptotes. The product $x \times y$ is constant for all points on the graph. A graph of $\frac{1}{y}$ vs. x or y vs. $\frac{1}{x}$ yields a straight line directed at the origin.
Example: pressure of a gas at various volumes</td>
<td>Straight line but not through the origin.
Example: volume of gas vs. Celsius temperature</td>
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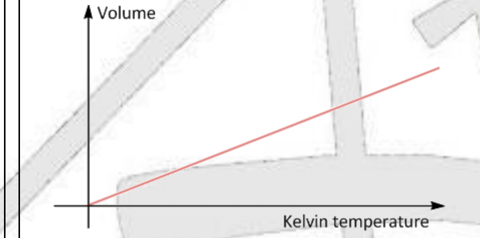
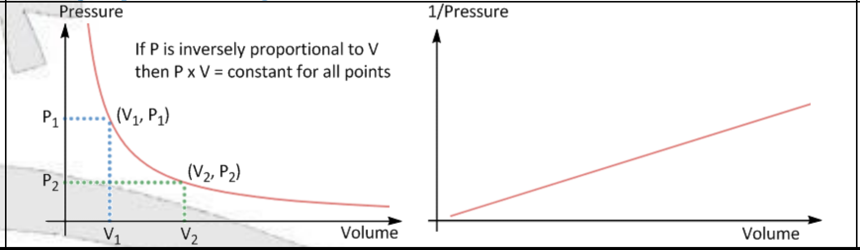
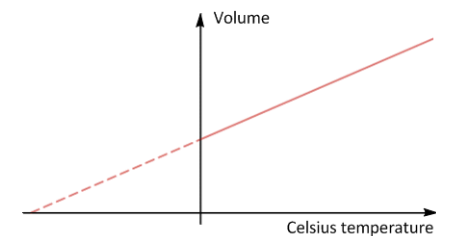
<tr>
<td> </td>
<td> </td>
<td> </td>
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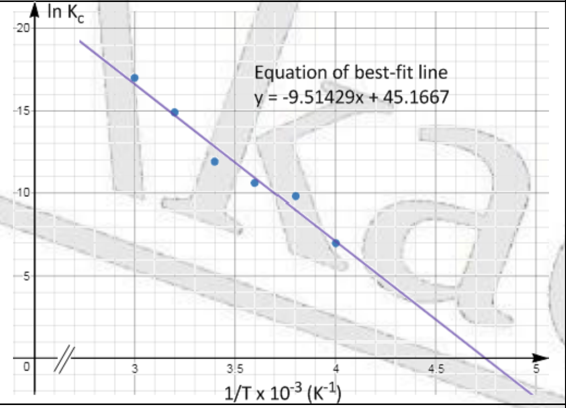
<tr>
<td>11.2</td>
<td>Graphical analysis – unfamiliar situation (these happen to be HL only)</td>
<td>
Exams may present unfamiliar situations and ask students to deduce the value of physical and chemical constants by associating theoretical mathematical relationships with plotted quantities.
<table>
<tr><th>Situation</th><th>Graph</th><th>Questions</th><th>Suggested answers</th></tr>
<tr>
<td rowspan="2">A student carries out a reversible reaction at various tempertures, and determines the K_c values at each temperature. The student produces a plot of $\ln K_c$ vs. $\frac{1}{T}$.</td>
<td rowspan="2"> </td>
<td>By considering two separate equations involving ΔG, explain why a plot of $\ln K_c$ vs $\frac{1}{T}$ produces a straight line.</td>
<td>By combining $\Delta G = -RT \ln K_c$ and $\Delta G = \Delta H - T\Delta S$, we can write $\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$. As ΔH and ΔS are typically independent of temperature, comparing this equation to the general straight line equation $y = mx + c$ can allow us to see that a plot of $\ln K_c$ vs. $\frac{1}{T}$ should yield a straight line whose gradient represents $-\frac{\Delta H}{R}$ and whose y–intercept represents $\frac{\Delta S}{R}$.</td>
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<tr>
<td>Hence use suitable graphical features to determine the values of ΔH and ΔS of the reaction.</td>
<td>The gradient of the plot represents $-\frac{\Delta H}{R}$.
Hence $\Delta H = -9.51 \times 1000 \times 8.31 = 79100\ J\ mol^{-1}$
$= 79.1\ kJ\ mol^{-1}$
The y–intercept of the plot represents $\frac{\Delta S}{R}$.
Hence $\Delta S = 45.17 \times 8.31 = 375\ J\ mol^{-1} K^{-1}$.</td>
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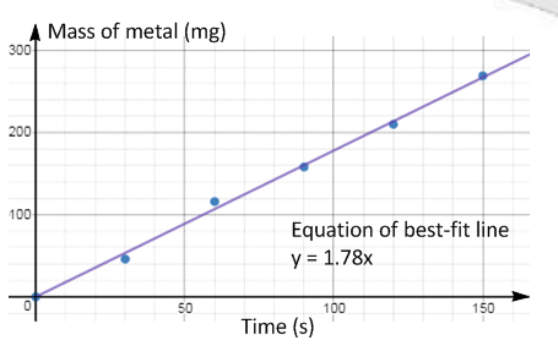
<td rowspan="2">A student electrolyses a solution of a transition metal nitrate using a 5.0–amp current, and records the mass of the metal collected over different time periods. The charge of the metal is known to be 3+.</td>
<td rowspan="2"> </td>
<td>By considering the mathematics behind electrolysis, determine the meaning of the gradient of the plot.</td>
<td>The mathematical equations for electrolysis yield of a 3+ cation are $Q = It$, $mol(e) = \frac{Q}{96500}$, $mol(metal) = \frac{mol(e)}{3}$ and $mass(metal) = mol(metal) \times M_r$. These equations can be combined to give an equation in terms of mass of metal, in mg:
$Mass = M_r \times mol(metal) \times 1000$
$= M_r \times \frac{mol(e)}{3} \times 1000 = M_r \times \frac{Q}{3 \times 96500} \times 1000 = M_r \times \frac{1000It}{3 \times 96500}$
Hence a plot of mass (in mg) vs. t should be a straight line through the origin with the value of the gradient corresponding to $\frac{1000IM_r}{3 \times 96500}$.</td>
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<tr>
<td>Hence suggest the identity of the metal.</td>
<td>Using the gradient of 1.78 and the current of 5.0 Amps, we have $1.78 = \frac{1000 \times 5.0 \times M_r}{3 \times 96500}$ leading to $M_r = 103$, and the closest match for this value of is rhodium ($M_r = 102.91$).</td>
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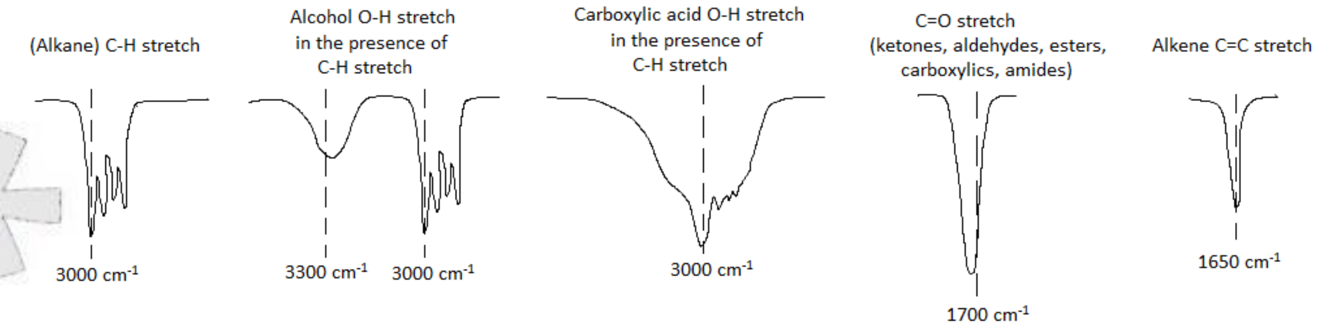
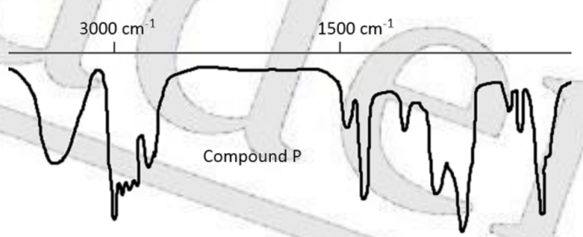
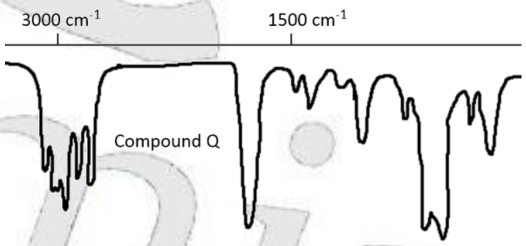
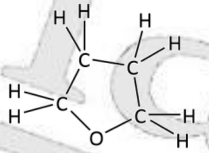
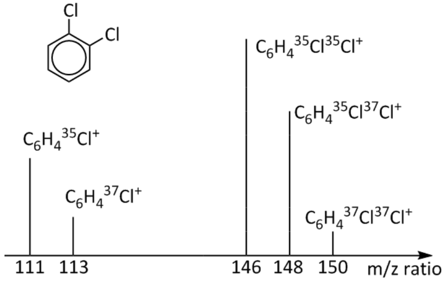
11.3	Infrared spectroscopy	Infrared spectroscopy is a spectroscopic technique that is based on IR radiation causing different types to bonds to undergo asymmetric molecular vibrations (stretching of bonds and distortion of bond angles) that would lead to a dipole (or polarity) change. Infrared radiation absorption is also the underlying mechanism for greenhouse gases causing the greenhouse effect.  In organic chemistry, IR spectroscopy is an excellent tool for identifying functional groups present in organic molecules, especially those involving a C=O and/or an O–H bond, as different molecular vibrations are caused by different frequencies / wavelengths within the IR region. The x–axis of an IR spectrum shows "wavenumber", a quantity that is the reciprocal of wavelength and is hence directly proportional to the energy of the absorption. Table 26 of the IB data booklet provides typical absorption wavenumbers of certain bonds. However, **Akademia experts suggest that it will be of your best interest to memorise the typical appearance (and not just the wavenumbers) of the peaks due to absorption by bonds within typical functional groups**. Also, notice that a "peak" in an infrared spectrum is actually a trough, formed due to the absorption of IR radiation, and is directed downwards. Strategies in analyzing an IR spectrum involve not just the recognition of the patterns above, but also the incorporation of IR spectroscopic knowledge during the speculation of organic structures that are consistent with information obtained using other types of analytical techniques, as well as chemical reactivity information. Also, students should bear in mind that negative inference is often useful – the absence of the peaks above can be linked to the absence of certain function groups within the compound, which allows you to rule out the presence of certain bonds or functional groups. Worked example. A compound P with formula $C_4H_{10}O$ reacts with excess acidified potassium dichromate(VI) to produce compound Q. Their IR spectra are shown below. Deduce the identities of the two compounds. Suggested answer: The broad peak at about 3200 cm^{-1} (OH stretch) suggests that P is an alcohol. Excess acidified potassium dichromate oxidizes a primary alcohol to a carboxylic acid and a secondary alcohol into a ketone. Since compound Q has a fairly sharp set of peaks at 2950 cm^{-1}, we can rule out the presence of a carboxylic acid OH, and conclude that Q must be a ketone – this is supported by the strong peak at 1700 cm^{-1} due to C=O stretch. The only $C_4H_{10}O$ isomer that is a secondary alcohol is butan–2–ol (P), and Q should be butanone (the corresponding ketone).   Worked example. A compound of formula C_4H_8O lacks any peaks in the 3100+ cm^{-1} region as well as in the 1500–1750 cm^{-1} region. Suggest a possible structural formula. Suggested answer. The IR observations described above indicate the absence of O–H, C=C and C=O bonds. The compound is most likely a cyclic ether, with the ring structure accounting for the IHD of 1 and the ether accounting for the oxygen atom. 
11.3	Fingerprint region	The region in an IR spectrum with wavenumber below 1500 cm^{-1}, the fingerprint region contains many peaks that are difficult to analyse individually and provides little diagnostic information. However, in the presence of reference spectra, the identity of the compound can be unambiguously identified. When determining unknown organic structures during an exam, students are advised not to use any peaks in the fingerprint region as evidence to justify a proposed structure. The fingerprint region, nevertheless, contains some C–O and C–halogen stretching absorptions. If a question asks you to identify a labeled peak within the fingerprint region, then by all means refer to the formula booklet to determine the correct answer.

<table>
<tr><td>11.3</td><td>Mass spectrometry</td><td>Mass spectrometry is a technique that allows information about the molecular mass of a covalent compound to be obtained. Inside a mass spectrometer, a molecule is ionised upon electron impact from a highly–energetic electron beam. The ionised molecules will travel to a detector, with electric and magnetic effects causing ions of different mass–to–charge (m/z) ratio to be detected at different times or at different positions.</td></tr>
<tr><td>11.3</td><td>Molecular ion peak</td><td>The molecular ion is the ion that is formed when a molecule loses an electron upon impact by a high–energy beam of electrons. For molecules that do not have isotopomers, the <u>molecular ion peak</u> on a mass spectrum is often denoted as M^+, and <u>is the peak with the largest mass–to–charge (m/z) ratio.</u> <u>The m/z value of this peak corresponds to the molecular mass of the original compound.</u>

Chlorinated and brominated compounds will show “chlorine and bromine signatures” within their mass spectra, due to the approximate 3 : 1 ^{35}Cl : ^{37}Cl isotopic distribution and approximate 1 : 1 ^{79}Br : ^{81}Br isotopic distribution. Dichloro– and dibromo compounds will show 9 : 6 : 1 and 1 : 2 : 1 signatures, respectively. Students are encouraged to use a probability tree diagram to explain the origin of these signatures.

Worked example. The mass spectrum of an aromatic organic compound possesses three peaks at m/z = 146, 148 and 150 with a relative intensity of 9 : 6 : 1. Suggest a possible molecular formula for the compound.
Suggested answer. The 9 : 6 : 1 ratio is a signature for the presence of two chlorine atoms within the compound. Taking away the mass of two ^{35}Cl atoms from 146 (the mass of the lightest isotopmer) means that the remaining mass = 146 – 2 × 35 = 76, and the most likely identity of the remaining atoms within the molecule is C_6H_4. Hence a possible molecular formula of the compound is $C_6H_4Cl_2$.

Mass spectrum of 1,2–dichlorobenzene, $C_6H_4Cl_2$, showing 3 molecular ion peaks in the form of a 9 : 6 : 1 dichloro– signature, as well as the 3 : 1 signature of a monochloro– fragment (fragmentation is elaborated in the next section)

 </td></tr>
<tr><td>11.3</td><td>Fragmentation</td><td>Fragmentation refers to a process that involves the formation of unstable cationic fragments due to the breaking of certain bonds within larger cations, when a compound is analyzed inside a mass spectrometer. Students should be aware that C–C bonds and C–O bonds often undergo fission inside a mass spectrometer to produce analyzable fragments. Table 28 of the formula book provides math AISL students with some differences of m/z values that correspond to the loss of some common organic fragments.

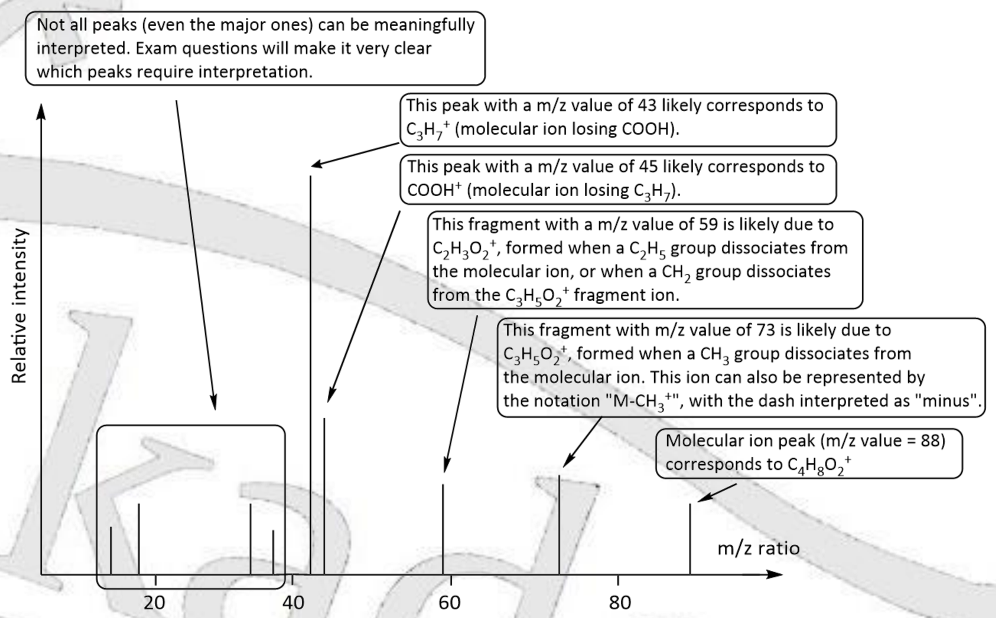
<table>
<tr><th>m/z value difference</th><th>Fragment lost</th></tr>
<tr><td>14</td><td>$–CH_2–$</td></tr>
<tr><td>15</td><td>$–CH_3$</td></tr>
<tr><td>17</td><td>–OH</td></tr>
<tr><td>18</td><td>H_2O</td></tr>
<tr><td>28</td><td>–C(=O)–</td></tr>
</table>
<table>
<tr><th>m/z value difference</th><th>Fragment lost</th></tr>
<tr><td>29</td><td>–CHO or $–C_2H_5$</td></tr>
<tr><td>31</td><td>$–OCH_3$</td></tr>
<tr><td>43</td><td>$–C_3H_7$, $–C(=O)CH_3$</td></tr>
<tr><td>45</td><td>–COOH</td></tr>
<tr><td></td><td></td></tr>
</table>

The exact fragmentation pattern of a compound depends on many physical and chemical factors, and is essentially unpredictable. Nevertheless, fragments of higher chemical stability, such as tertiary carbocations and resonance–stabilised acylium (RCO^+) carbocations, tend to be more abundant inside the mass spectrometer, and produce more intense peaks within a mass spectrum.

Fragmentation can be represented by chemical equations. For example, the compound ethyl ethanoate ($CH_3COOCH_2CH_3$) can first become the molecular ion $CH_3COOCH_2CH_3^+$, which can then undergo fragmentation at any position. For example, fragmentation at the C–O single bond can occur in two different ways – they are represented by following equations:
$CH_3COOCH_2CH_3^+ \rightarrow CH_3CO^+ + OCH_2CH_3\bullet$
$CH_3COOCH_2CH_3^+ \rightarrow CH_3CO\bullet + OCH_2CH_3^+$

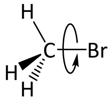
Keep in mind that only charged fragments are detectable inside a mass spectrometer. Thus, the first fragmentation reaction above produces a fragment peak at a m/z value of 43 (corresponding to CH_3CO^+) while the second fragmentation reaction produces a fragment peak at a m/z value of 45 (corresponding to $OCH_2CH_3^+$).
Also, <u>when identifying fragments during an exam question, students must remember to include the positive charge.</u>

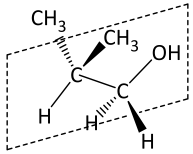
Worked example. The mass spectrum of a compound $C_5H_{12}O$ shows a significant peak at m/z ratio of 45. Determine the identity of this peak.
Suggested answer. The molecular mass of $C_5H_{12}O$ is 88, and a top–down approach can reveal that a fragment of mass = 88 – 45 = 43 has been lost.
According to the common fragment table, the fragment lost could be $–C_3H_7$, or $–C(=O)CH_3$.
The structural formula is not provided. However, an IHD analysis shows that $C_5H_{12}O$ is fully saturated, and the $–C(=O)CH_3$ fragment could not have been present within the molecule.
Therefore, the only fragment that can be reasonably lost from $C_5H_{12}O$ is $–C_3H_7$, and the identity of the peak is $C_2H_5O^+$.</td></tr>
</table>

11.3	Analysing a mass spectrum	There are two strategies that are commonly used to assign mass spectral peaks. A top–down approach involves deducing the fragment lost from the molecular ion, and is more suitable to analyze high m/z value fragments. A bottom–up approach is more suitable for analyzing small fragments. In general, the top–down approach is more useful in solving for the structural formula of an unknown compound. Shown here is a partially annotated mass spectrum of butanoic acid, $CH_3CH_2CH_2COOH$ ($C_4H_8O_2$) Notice that most of the important peaks can be attributed to the loss of identifiable fragments from the molecular ion or from bigger fragments.  Not all peaks (even the major ones) can be meaningfully interpreted. Exam questions will make it very clear which peaks require interpretation. This peak with a m/z value of 43 likely corresponds to $C_3H_7^+$ (molecular ion losing COOH). This peak with a m/z value of 45 likely corresponds to $COOH^+$ (molecular ion losing C_3H_7). This fragment with a m/z value of 59 is likely due to $C_2H_3O_2^+$, formed when a C_2H_5 group dissociates from the molecular ion, or when a CH_2 group dissociates from the $C_3H_5O_2^+$ fragment ion. This fragment with m/z value of 73 is likely due to $C_3H_5O_2^+$, formed when a CH_3 group dissociates from the molecular ion. This ion can also be represented by the notation "M-CH_3^+", with the dash interpreted as "minus". Molecular ion peak (m/z value = 88) corresponds to $C_4H_8O_2^+$ A more adventurous exam question will instead provide you with chemical reactivity information in addition to spectral data, and ask you to back–deduce the identity of the compounds. Worked example. Compound P is a secondary alcohol of molecular formula $C_5H_{12}O$. Compound P reacts with acidified potassium dichromate(VI) to give compound Q with a molecular formula of $C_5H_{10}O$. The mass spectrum of compound Q shows significant peaks at m/z values of 86, 71, 57 and 29, but no peaks at m/z value of 43. Determine the most likely structural formula of compound P and Q. Suggested answer: • Realise that compound Q must be a ketone, because a ketone is what a secondary alcohol becomes when treated with acidified potassium dichromate(VI). • Realise that the fragments with m/z value of 71 and 57 are likely formed when a CH_3 and C_2H_5 are lost from the molecular ion, respectively. Hence an ethyl group (C_2H_5) was likely present in Q. Note that the fragment ion with m/z 57 cannot be produced by the loss of –CHO from the molecular ion, as compound Q is a ketone and does not possess the –CHO (aldehyde) functional group. • Interpret the lack of fragment at m/z value of 43 to the absence of groups such as C_3H_7 or CH_3CO. Hence we can rule out structures such as $CH_3COC_3H_7$ (pentan–2–one or 3–methylbutan–2–one) • The only possible $C_5H_{10}O$ ketone that satisfies the mass spectral data is pentan–3–one ($CH_3CH_2COCH_2CH_3$), hence compound P must be the precursor alcohol pentan–3–ol, $CH_3CH_2CH(OH)CH_2CH_3$.
21.1	X–ray crystallo–graphy	X–ray crystallography is an analytical technique that involves shining X–rays (at many different angles) at a single crystal of a substance, and analyzing the diffraction patterns of the X–rays (due to the electrons) in order to locate the position of the atomic nuclei, and hence elucidate the structure of a typically novel (newly discovered) compound. X–Ray crystallography can be used to reliably identify the bond lengths and bond angles of compounds, and can be attributed to the huge advances of many fields of chemistry e.g. VSEPR theory, hence the increased suffering of chemistry students.

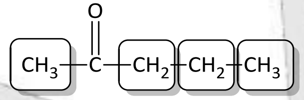
<table>
<tr>
<td>11.3</td>
<td>Proton (^1H) NMR spectroscopy</td>
<td>
NMR spectroscopy is a spectroscopic technique that is based on <u>radio waves</u> causing nuclear spin energy level transitions.

^1H NMR is excellent for deducing the carbon skeleton in organic molecules. Specifically, the 4 pieces of information available are……
i) number of types of proton chemical environments (number of signals)
ii) relative number of protons in each environment (from integration trace);
iii) nature of proton environments (from chemical shift);
iv) coupling patterns due to non–equivalent protons on adjacent carbons (HL only)

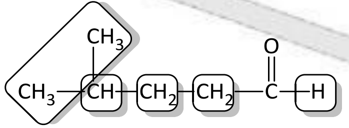
Note that i) and ii) are information that NEVER LIES, while iii) and iv) are not 100% reliable, especially in the presence of other stronger pieces of evidences such as i), ii) and/or mass–spectral and IR data.
</td>
</tr>
<tr>
<td>11.3</td>
<td>Chemical environment</td>
<td>
The number of chemical environments is the number of different types of hydrogen atoms present within the structural formula. Two hydrogen atoms, or two groups of hydrogen atoms, are <u>equivalent</u> i.e. have the same chemical environment if……
• Their positions within the structural formula are interchangeable by bond rotation, (e.g. CH_3–) or
• They are related to each other by an internal mirror plane of reflection (e.g. CH_2Cl_2, $CH_3CH_2OCH_2CH_3$, the CH_3s of 2–methylpropan–1–ol)




Worked example. Determine the number of chemical environments within the following compounds.

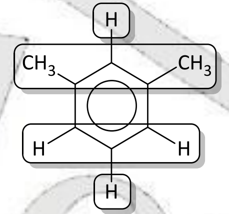
<table>
<tr><th>Common math AISL struggles</th><th>Analysis</th></tr>
<tr><td>Recognizing non–identical CH_2s (pentan–2–one)
 </td><td>There are 4 types of environments.

The terminal CH_3s are not identical.

The internal CH_2s are not identical, either.</td></tr>
<tr><td>Recognizing internal plane symmetry (4–methylpentanal)
 </td><td>There are 5 types of environments.

The “4–methyl” CH_3 is equivalent to the terminal CH_3 as they are related by an internal mirror reflection plane.

The internal CH_2s are not identical.</td></tr>
</table>

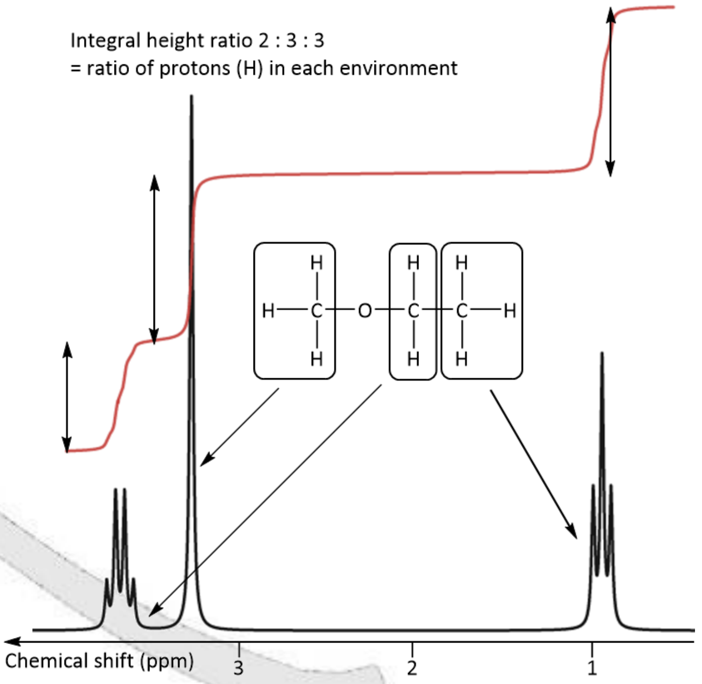
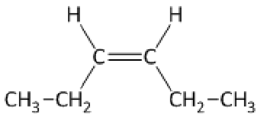
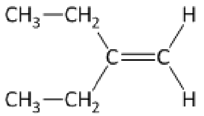
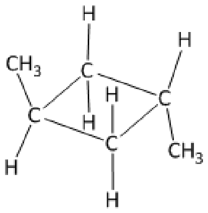
<table>
<tr><th>Common math AISL struggles</th><th>Analysis</th></tr>
<tr><td>Substituted benzene ring (1, 3–dimethylbenzene)
 </td><td>There are 4 types of environments.

The two CH_3 groups are related by internal mirror plane.

The hydrogens on carbon–4 and carbon–6 are also related by an internal mirror plane of reflection.

The hydrogens on carbon–2 and carbon–5 are unique.</td></tr>
</table>

<u>One type of environment gives rise to one signal</u>. Students should nevertheless be aware of the following situations:
• It’s possible that the signals due to non–equivalent protons overlap and are unresolved from each other, due to hydrogen atoms having very similar chemical environments. This will be addressed in the “chemical shift” section.
• A peak may be split into a multiple–line fine pattern due to spin–spin coupling (HL). In this situation, the word “peak” still refers to the entire fine–line pattern, and not the individual peaks within the fine pattern.
</td>
</tr>
</table>

11.3	Integration trace	Integration provides information regarding the area under each peak pattern. These area ratios correspond to the ratio of the protons within each type of environment. Areas can be presented as separate integrals, or a single integral trace that indicates the cumulative area. Typical integration values observed in a ^1H NMR spectrum are as follows: A 2–proton peak often corresponds to a $-CH_2-$, or two equivalent H related by molecular symmetry; A 3–proton peak often corresponds to a CH_3-; A 6–proton peak often corresponds to two equivalent CH_3- related by molecular symmetry; A 9–proton peak often corresponds to $(CH_3)_3C-$. For analysis purposes, there may be no need to distinguish between certain types of non–equivalent protons. For example, the 5 protons of a phenyl (C_6H_5) group, or the 4 protons on a di–substituted benzene ring ($-C_6H_4-$) are sometimes presented as one single type of environment with an integration of 5 and 4, respectively. The ratio of protons within each type of environment can be determined by using a ruler to measure the heights of integrals presented on a ^1H NMR spectrum. Consider the ^1H NMR spectrum of methoxyethane, as shown to the right.  Worked example. A compound with formula $C_5H_{11}Br$ has 3 signals, and an integration trace whose integral lengths are 1.0, 1.5 and 3.0 cm, respectively. Determine a possible structural formula of this compound. Suggested answer: the peak integral trace length of 1.0 cm corresponds to $11 \times \frac{1.0}{1.0+1.5+3.0} = 2$ protons. Similarly, the 1.5–cm integral and 3.0–cm integral correspond to a 3–proton and 6–proton peak, respectively. We likely have the pieces CH_3 (3–proton peak), $-CH_2-$ (2–proton peak), $-C(CH_3)_2-$ and $-Br$ to work with. The only 2 reasonable ways to connect these pieces are $CH_3-C(CH_3)_2-CH_2-Br$ and $CH_3-CH_2-C(CH_3)_2-Br$, respectively. The first structure results in the CH_3 and $-C(CH_3)_2-$ becoming 9 equivalent protons, which means it should be ruled out. Hence the only structural formula of $C_5H_{11}Br$ that satisfies the ^1H NMR information above would be $CH_3-CH_2-C(CH_3)_2-Br$ i.e. 2–bromo–2–methylbutane. Worked example. Determine the integration ratio of peaks in the ^1H NMR spectrum of pentan–2–one and pentan–3–one, respectively. Suggested answer: Pentan–2–one exhibits 4 proton environments in a 3 : 2 : 2 : 3 ratio while pentan–3–one contains two proton environments in a 6 : 4 ratio. Accordingly, the integration ratio for pentan–2–one will be the same as the environment ratio of 3 : 2 : 2 : 3, while the integration ratio observed in pentan–3–one will be the simplest integer ratio, which is 3 : 2. Worked example. A molecule with empirical formula CH_2 and $M_r = 84.18$ has 3 peaks in its proton NMR spectrum with an integration ratio of 3 : 2 : 1. Determine a possible structural formula. Suggested answer. An empirical formula analysis ($\frac{84.18}{12.01+2.02} = 6$) reveals that the molecular formula is $(CH_2)_6$, or C_6H_{12}, and the 3 : 2 : 1 ratio indicates that there are 6 of 1 type of proton, 4 of a second type of proton, and 2 of a third type of proton. Some trial and error can allow you to deduce the following structures as valid answers: hex-3-ene (cis or trans) 2-ethylbut-1-ene trans-1,3-dimethylcyclobutane

11.3

Parts per million (Chemical shift, δ)

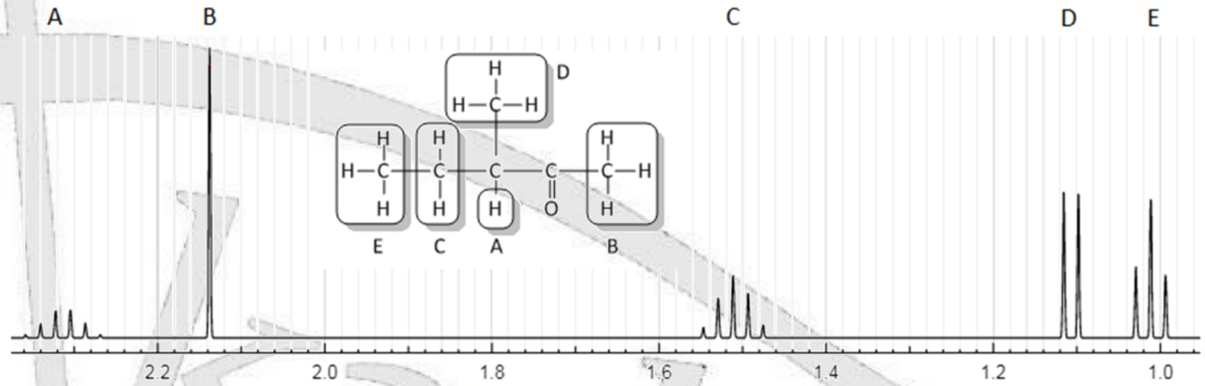
Measured in parts per million, the chemical shift is the horizontal–axis quantity on an NMR spectrum that provides information regarding the chemical environments of protons within an organic compound. The terms “upfield” and “downfield” are used to refer to small and large chemical shift values, respectively. Unlike a traditional x–axis, the NMR ppm scale features large values located on the left, while small and negative values are located to the right.

Chemical shifts of organic compounds are often measured against the chemical shift of tetramethylsilane (TMS; $Si(CH_3)_4$). TMS is used as a chemical shift reference – a small amount of TMS is often added to NMR samples for a few reasons:

- It is unreactive and low boiling – it will not alter the identity of the compound, and will allow the recovery of the compound;
- It is non–toxic, unlike most IB students;
- Its chemical shift, defined to be 0 ppm, is far away from the chemical shifts of typical organic compounds, hence the TMS peak rarely obscures other peaks;
- It only has one peak, which also reduces the likelihood of the TMS peak obscuring other relevant peaks.

The ^1H NMR chemical shift table provided in the booklet can be misleading without proper interpretation, which are provided here by Akademia experts:

Proton type according to IB	What this really means	IB Chemical shift (ppm)	Akademia Expert’s interpretation
$-CH_3$	Primary (methyl) CH_3 with no immediate functional group next to it	0.9 – 1.0	A CH_3 group often appears at 0.9 – 1.0 (ppm), but don’t be surprised if you see it at 1.2 or 1.3, either.
$-CH_2-R$	Secondary CH with no immediate functional groups next to it	1.3 – 1.4	A secondary CH with no neighbouring functional group often appears within this range.
$-CHR_2$	Tertiary CH with no immediate functional groups next to it	1.5	A tertiary CH with no neighbouring functional group often appears within this range.
$ROC(=O)CH_2-$	CH next to the C=O of a carboxylic acid or ester. Can be methyl, a primary, secondary or tertiary CH, despite IB showing CH_2 in the structure.	2.0 – 2.5	The chemical shift tends to be at the lower end of the range for primary CH (methyl) and higher for tertiary CH. The chemical shift is also subject to change (downfield shift) due to the presence of other functional groups.
$RC(=O)CH_2-$	CH next to the C=O of an aldehyde or a ketone. Can be methyl, a primary, secondary or tertiary CH, despite IB showing CH_2 in the structure.	2.2 – 2.7	The chemical shift tends to be lower for primary CH (methyl) and higher for tertiary CH. Also note that this range is similar to the range in the previous entry. Extra data such as empirical formula or MS should help distinguish between these two. Finally, The chemical shift is also subject to change due to the presence of other functional groups.
$R-C_6H_4-CH_3$	CH next to a benzene (phenyl) ring. Can be methyl, a primary, secondary or tertiary CH, despite IB showing CH_3 in the structure.	2.5 – 3.5	The chemical shift tends to be at the lower end of the range for primary CH (methyl) and higher for tertiary CH, and is also subject to change due to the presence of other functional groups.
$-C\equiv C-H$	CH on a C≡C	1.8 – 3.1	
$-CH_2-Hal$	CH next to a halogen atom. Can be methyl, a primary or secondary CH, despite IB showing CH_2 in the structure.	3.5 – 4.4	1. The chemical shift tends to be at the lower end of the range for primary CH (methyl) and higher for secondary CH. 2. The chemical shift tends to be higher for chloroalkanes and lower for iodoalkanes. 3. The chemical shift will go further downfield if there are multiple halogens. For example, the proton signal of CH_2Cl_2 appears at a chemical shift of 5.2 ppm while for $CHCl_3$, the proton signal appears at 7.3 ppm.
$R-O-CH_2-$	CH next to an alcohol or ether oxygen atom. Can be methyl, a primary or secondary CH, despite IB showing CH_2 in the structure.	3.3 – 3.7	The chemical shift tends to be at the lower end of the range for primary CH (methyl) and higher for secondary CH. The chemical shift is also subject to change due to the presence of other functional groups.
$RC(=O)-O-CH_2-$	CH next to the C—O of an ester. Can be methyl, a primary or secondary CH, despite IB showing CH_2 in the structure.	3.7 – 4.8	The chemical shift tends to be at the lower end of the range for primary CH (methyl) and higher for secondary CH. The chemical shift is also subject to change due to the presence of other functional groups, as always.
RCOOH	Carboxylic acid OH	9.0 – 13.0	This peak may be broad and unobservable if some acid–base–active solvent (e.g. water) is used
ROH	Alcohol OH peak	1.0 – 6.0	This peak can be all over the place, and can also be broad due to acid–base exchange reactions with acid–base–active solvents such as water. The alcohol IR absorption is way more distinctive and diagnostic.
$-HC=CH_2$	Alkene CH	4.5 – 6.0	The chemical shift tends to be lower for primary CH (methyl) and higher for tertiary CH.
$R-C_6H_4-OH$	Phenol (benzene alcohol) OH	4.0 – 12.0	
$R-C_6H_4-H$	CH on a benzene ring. The CH can be on any position within the ring, despite IB showing the H to be directly across the other bonding opening with the benzene ring.	6.9 – 9.0	
$RC(=O)H$	Aldehyde CH	9.4 – 10	

<table>
<tr>
<td>21.1</td>
<td>Spin–spin coupling</td>
<td>
<p>Coupling is a situation during which the presence of n non–equivalent protons on neighbouring (carbon) atoms results in a signal being split into an n+1 line fine pattern, with relative intensity within the pattern obeying the Pascal's triangle.</p>
<p>Unsplit signals are called singlets. Typical patterns are doublets, triplets, quartets. More complex patterns (5: quintet, 6: hextet, 7: heptet) can be referred to as multiplets on exams.</p>
<p>Spin–spin coupling splitting patterns are most reliable for C–H on tetrahedral (sp^3) carbons and C–H on benzene rings. On the other hand, spin–spin coupling splitting patterns are not necessarily observed, or difficult to interpret, for alkene H, aldehyde H and alcohol H.</p>
<p>Worked example. Explain the spin–spin coupling patterns for each signal of 3–methylpentan–2–one, $CH_3C(O)CH(CH_3)CH_2CH_3$. (Image produced using NMR simulator: http://www.nmrdb.org/new_predictor/index.shtml?v=v2.95.0)</p>


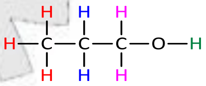
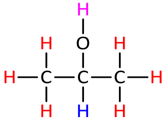
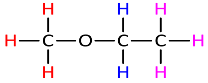
<p>Suggested answers:</p>
<table>
<tr><th>Signal</th><th>Description</th><th>Relativity intensity of peaks within the fine pattern</th><th>Proton(s) responsible for this signal</th><th>Proton(s) that causes the formation of the observed splitting pattern</th></tr>
<tr><td>A</td><td>Multiplet or hextet</td><td>1 : 5 : 10 : 10 : 5 : 1</td><td>$CH_3C(O)C\underline{H}(CH_3)CH_2CH_3$</td><td>C and D</td></tr>
<tr><td>B</td><td>Singlet</td><td>1</td><td>$C\underline{H_3}C(O)CH(CH_3)CH_2CH_3$</td><td>None</td></tr>
<tr><td>C</td><td>Multiplet or quintet</td><td>1 : 4 : 6 : 4 : 1</td><td>$CH_3C(O)CH(CH_3)C\underline{H_2}CH_3$</td><td>E and A</td></tr>
<tr><td>D</td><td>Doublet</td><td>1 : 1</td><td>$CH_3C(O)CH(C\underline{H_3})CH_2CH_3$</td><td>A</td></tr>
<tr><td>E</td><td>Triplet</td><td>1 : 2 :1</td><td>$CH_3C(O)CH(CH_3)CH_2C\underline{H_3}$</td><td>C (2 protons, 2 + 1 = 3)</td></tr>
</table>
</td>
</tr>
</table>

11.3, 21.1

Analyzing ^1H NMR spectral data

Many ^1H NMR spectroscopic features can effectively help distinguish between compounds, or eliminate wrong structures in leading to the correct structural formula when a molecular formula is given.

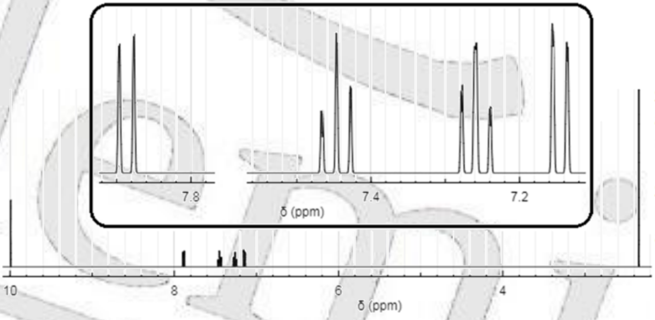
Worked example. Propan–1–ol ($CH_3CH_2CH_2OH$), propan–2–ol ($CH_3CH(OH)CH_3$) and methoxyethane ($CH_3OCH_2CH_3$) are isomers of each other. Explain how ^1H NMR spectroscopy can be used to distinguish between samples of propan–1–ol, propan–2–ol and methoxyethane ($CH_3OCH_2CH_3$).
Suggested answers:

Compound	Propan–1–ol	Propan–2–ol	Methoxyethane
Displayed formula			
Number of peaks	4	3	3
Relative area under each peak	3 : 2 : 2 : 1	6 : 1 : 1	3 : 2 : 3 (or 3 : 3 : 2; order does not matter)
Possible chemical shifts for each peak (ppm)	$\underline{CH_3}CH_2CH_2OH$: 0.9 – 1.0 $CH_3\underline{CH_2}CH_2OH$: 1.3 – 1.4 $CH_3CH_2\underline{CH_2}OH$: 3.3 – 3.7 $CH_3CH_2CH_2\underline{OH}$: 1.0 – 6.0	$\underline{CH_3}CH(OH)\underline{CH_3}$: 0.9 – 1.0 $CH_3\underline{CH}(OH)CH_3$: 3.3 – 3.7 $CH_3CH(\underline{OH})CH_3$: 1.0 – 6.0	$\underline{CH_3}OCH_2CH_3$: 3.3 – 3.7 $CH_3O\underline{CH_2}CH_3$: 3.3 – 3.7 $CH_3OCH_2\underline{CH_3}$: 0.9 – 1.0
Splitting pattern for each peak	$\underline{CH_3}CH_2CH_2OH$: triplet $CH_3\underline{CH_2}CH_2OH$: hextet/multiplet $CH_3CH_2\underline{CH_2}OH$: quartet if coupling to OH observed, triplet if not observed $CH_3CH_2CH_2\underline{OH}$: triplet if coupling to CH_2 observed, singlet if not observed	$\underline{CH_3}CH(OH)\underline{CH_3}$: doublet $CH_3\underline{CH}(OH)CH_3$: multiplet (octet if coupling to OH observed, heptet if not observed) $CH_3CH(\underline{OH})CH_3$: doublet if coupling to CH observed, singlet if not observed.	$\underline{CH_3}OCH_2CH_3$: singlet $CH_3O\underline{CH_2}CH_3$: quartet $CH_3OCH_2\underline{CH_3}$: triplet

More adventurous exam questions will instead provide you with spectral data and ask you to back–deduce the structural formula of a compound. The key to solving such problems is to keep developing identities of fragments, based on number of peaks and integration (information that never lies) that are all consistent with the other spectral data (such as splitting and chemical shifts), as well as ruling out the wrong ones. (http://www.nmrdb.org/new_predictor/index.shtml?v=v2.95.0)

Worked example. A compound with empirical formula C_8H_8O and a molecular ion peak at m/z = 120 is analyzed by ^1H NMR spectroscopy, resulting in the following spectrum. Integration and detailed splitting patterns are also provided. Deduce the identity of this compound.
Suggested answer:

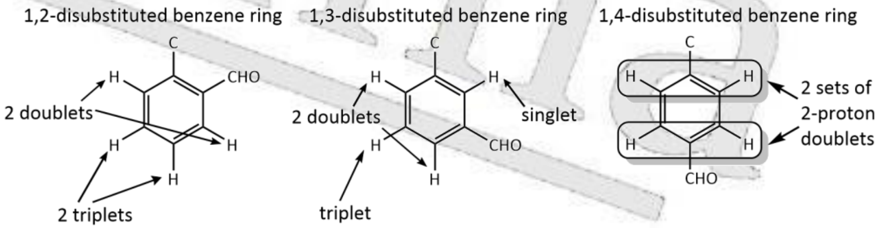
- Mass spectral data indicate that the molecular formula is the same as the empirical formula.
- The fully saturated version of a C_8 compound has $2(8) + 2 = 18$ hydrogens, hence the formula C_8H_8O corresponds to an IHD of $\frac{18-8}{2} = 5$. This, plus the fact that there are diagnostic peaks between 7 to 8 ppm (diagnostic essentially means "the peak cannot be mistaken for anything else unless you do math AISL"), suggests that a benzene ring (which contributes 4 to the IHD) is likely present.
- The 10.0 ppm peak is another highly diagnostic peak that indicates the presence of an aldehyde (–CHO), with the C=O bond (that's not directly observable using ^1H NMR otherwise) allowing us to completely account for the IHD value of 5.
- The fact that there are 4 1–proton peaks in the benzene region suggests that we have a di–substituted benzene ring ($–C_6H_4–$).
- The 2.35 ppm 3–proton singlet is a $CH_3–$, likely bonded to the benzene ring.
- At this stage we can connect the pieces: $CH_3–C_6H_4–CHO$. This formula accounts for all atoms, and is consistent with all ^1H NMR data that we have analyzed so far.



Integration (left to right):
1 : 1 : 1 : 1 : 1 : 3

Splitting pattern of peaks at 10.0 ppm and 2.35 ppm are singlets.

Splitting pattern of peaks between 7 ppm to 8 ppm are shown in the inset.



The only issue that we have not addressed is the positions of the functional groups on benzene ring. We now resort to the benzene ring proton splitting pattern, which will help delineate the position of the di–substitution. Shown to the right are the 3 possible isomers, and the splitting patterns that we anticipate. Hopefully it is clear to us that the 1,2–disubstituted benzene ring is the one who gives a splitting pattern that is consistent with the one observed in the spectrum. Therefore the unknown compound is 2–methylphenylmethanal (2–methylbenzaldehyde).