



Rewarding Learning

ADVANCED
General Certificate of Education
2022

Centre Number

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Candidate Number

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Chemistry

StemUp Model Solution

Assessment Unit A2 3

assessing

Further Practical Chemistry

Practical Booklet B (Theory)



[ACH32]

ACH32

TUESDAY 21 JUNE, MORNING

TIME

1 hour 15 minutes.

INSTRUCTIONS TO CANDIDATES

Write your Centre Number and Candidate Number in the spaces provided at the top of this page.

You must answer the questions in the spaces provided.

Do not write outside the boxed area on each page or on blank pages.

Complete in black ink only. **Do not write with a gel pen.**

Answer **all four** questions.

INFORMATION FOR CANDIDATES

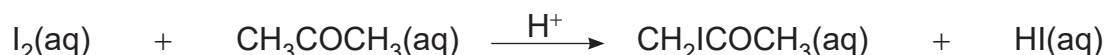
The total mark for this paper is 60.

Figures in brackets printed down the right-hand side of pages indicate the marks awarded to each question or part question.

A Periodic Table of Elements (including some data) is provided.



- 1 The kinetics of the reaction between iodine and propanone were investigated. The reaction is catalysed by hydrogen ions.



The influence of the iodine concentration on the reaction rate can be studied if large excesses of propanone and sulfuric acid are used. An experiment is carried out as follows:

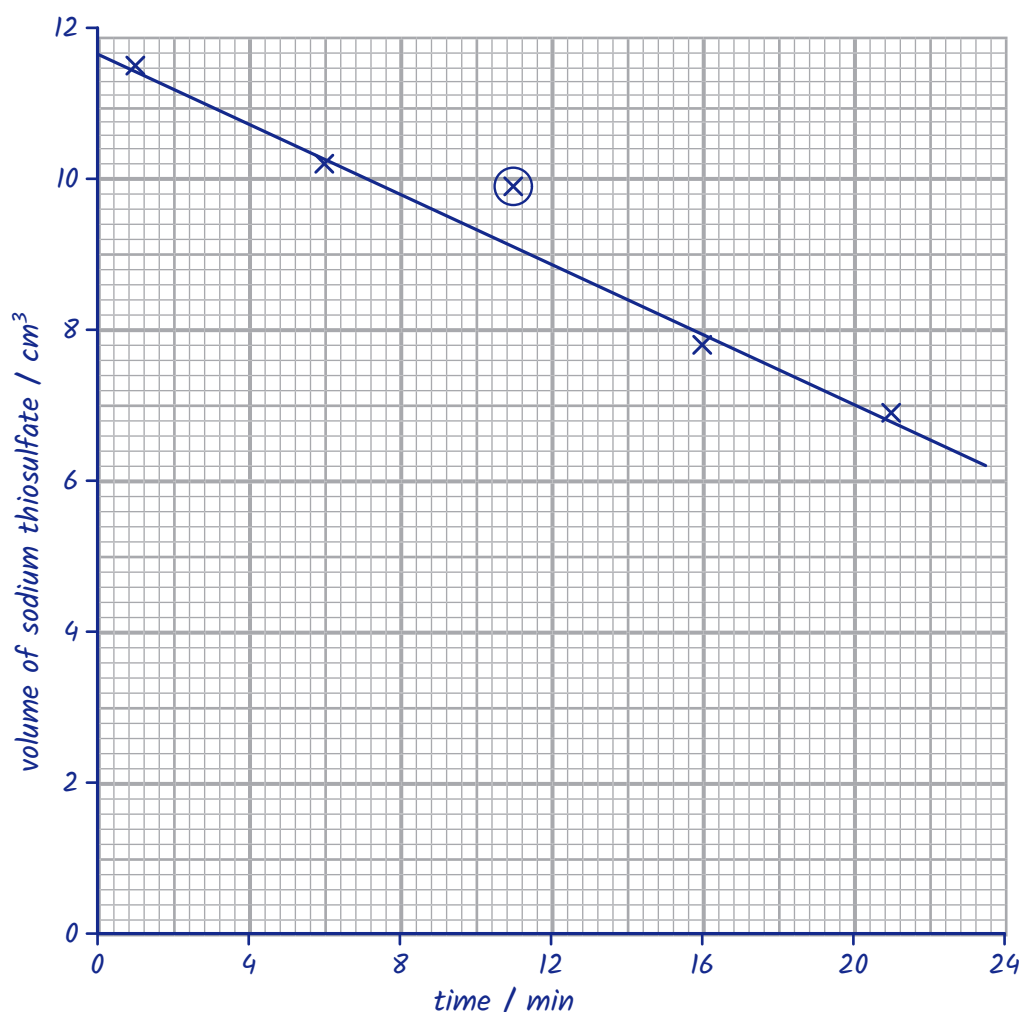
- 1 Mix 25.0 cm³ of 1.0 mol dm⁻³ propanone solution with 25.0 cm³ of 1.0 mol dm⁻³ sulfuric acid in a beaker.
- 2 Add 50.0 cm³ of 0.02 mol dm⁻³ iodine solution, stir the mixture and start a stopwatch.
- 3 Using a pipette, withdraw a 10.0 cm³ sample of the mixture and transfer it to a conical flask.
- 4 Add sodium hydrogencarbonate, with stirring, until the fizzing ceases. The time at which the sodium hydrogencarbonate is added is recorded.
- 5 Titrate the solution with 0.01 mol dm⁻³ sodium thiosulfate solution, using starch indicator.
- 6 Repeat steps 3–5 at five minute intervals.

The following results were obtained from the experiment:

Time /min	Volume of sodium thiosulfate solution /cm ³
1	11.5
6	10.2
11	9.9
16	7.8
21	6.9



- (a) Plot a graph of volume of sodium thiosulfate solution against time and draw a line of best fit.



[4]

- (b) Identify the anomalous result from the graph.

The reading at 11 min (9.9 cm³).

[1]

- (c) Suggest why using large excesses of propanone and sulfuric acid allows the order of reaction with respect to iodine to be deduced.

The concentrations of propanone and sulfuric acid remain effectively
constant, so only the iodine concentration changes.

[1]

[Turn over]

12886.02R



16ACH3203

- (d) Explain why sodium hydrogencarbonate is added to each sample.

It reacts with (neutralises) the sulfuric acid catalyst, which quenches (stops) the reaction at that time.

[1]

- (e) The graph can be used to deduce the order of reaction with respect to iodine.

- (i) Explain why a graph of volume of sodium thiosulfate solution against time can be used to deduce the order of reaction with respect to iodine.

The concentration of iodine is directly proportional to the volume of sodium thiosulfate solution.

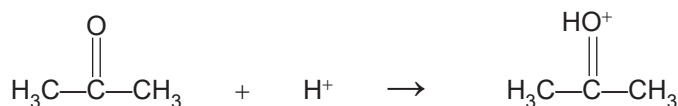
[1]

- (ii) State and explain the order of reaction with respect to iodine.

Zero order with respect to iodine, because the graph is a straight line (constant gradient, so the rate is constant).

[2]

- (iii) The following rate-determining step is proposed for the reaction:



Explain whether it is consistent with your answer to (e)(ii).

Consistent, as iodine does not appear in the proposed rate-determining step.

[1]



(f) Starch is added towards the end of each titration.

- (i) State the colour changes when starch is added to each flask and at the end point of each titration.

Colour change when starch is added to flask: straw (pale yellow)
to blue-black

Colour change at end point: blue-black to colourless

[2]

- (ii) Suggest why starch is not added at the start of each titration.

Iodine would form an irreversible (insoluble) complex with starch
at high concentration, so the end point would be inaccurate.

[1]

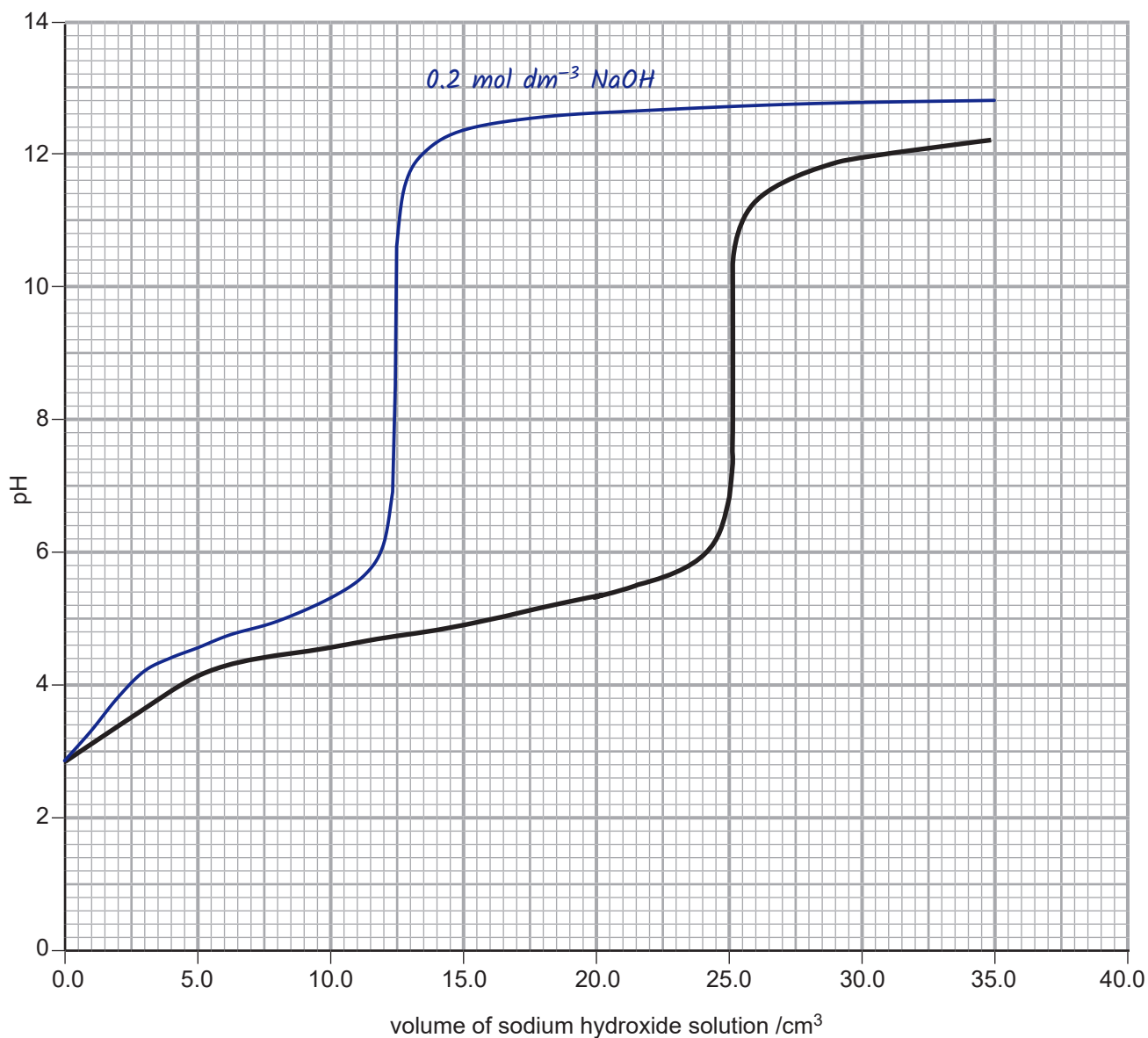
[Turn over]

12886.02R



16ACH3205

- 2 The pH curve shown below was obtained when 25.0 cm^3 of 0.1 mol dm^{-3} ethanoic acid were titrated against 0.1 mol dm^{-3} sodium hydroxide solution.



12886.02R



16ACH3206

- (a) (i) What volume of sodium hydroxide solution is required to neutralise half of the ethanoic acid in the titration?

12.5 cm³ [1]

- (ii) Use the pH curve to determine the pH of the mixture when the volume of sodium hydroxide solution in (a)(i) is added.

pH = 4.75 [1]

- (iii) At the pH in (a)(ii), [CH₃COOH] = [CH₃COO⁻]

Use your answer to (a)(ii) to determine the value of K_a for ethanoic acid. Give your answer to 3 significant figures.

pH = pK_a = 4.75, so K_a = 10^{-4.75}

K_a = 1.78 × 10⁻⁵ mol dm⁻³ [1]

- (b) On the axes, sketch the pH curve that would be obtained if 0.2 mol dm⁻³ sodium hydroxide solution was used in the titration. [2]

[Turn over]



- (c) When half of the ethanoic acid is neutralised by the sodium hydroxide solution, the resulting mixture can act as a buffer solution.

- (i) Define the term **buffer solution**.

A solution which resists changes in pH when small amounts of acid or alkali are added.

[1]

- (ii) Explain, using an ionic equation, how this solution acts as a buffer when alkali is added.



The added OH⁻ ions are removed by reacting with the ethanoic acid, so the pH stays almost constant.

[2]

- (d) Explain why a solution of sodium ethanoate has a pH above 7.

It is the salt of a weak acid and a strong base: $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$

[1]

- (e) The indicators bromophenol blue and thymol blue both exhibit the same colour change when used in acid-base titrations. Bromophenol blue changes colour in the pH range 3.0–4.5 and thymol blue changes colour in the pH range 8.0–9.6.

State and explain which indicator is suitable when 0.1 mol dm⁻³ ethanoic acid is titrated against 0.1 mol dm⁻³ sodium hydroxide solution.

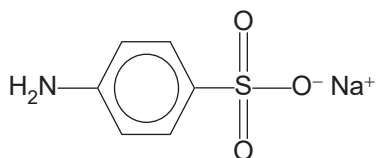
Thymol blue.

Its colour change range (pH 8.0 to 9.6) lies within the vertical section of the pH curve (about pH 7 to 11).

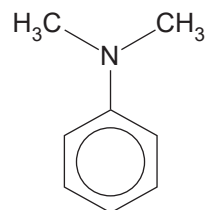
[2]



- 3 Methyl orange is an azo dye. It can be synthesised from sodium sulfanilate and N,N-dimethylaniline, which react in equimolar amounts in a coupling reaction.



sodium sulfanilate



N,N-dimethylaniline

The procedure below was used to synthesise methyl orange.

2.70 g of sodium sulfanilate were dissolved in deionised water and sodium nitrite was added. The solution was poured over crushed ice and concentrated hydrochloric acid was added. N,N-dimethylaniline (1.71 g, density = 0.956 g cm⁻³), in ethanoic acid was added to this diazonium ion and the solid crude product formed. The solid was removed from the solution by suction filtration. It was recrystallised using water as a solvent and 2.32 g of methyl orange were obtained. The melting point of the recrystallised methyl orange was determined. Pure methyl orange melts at 300°C.

- (a) Sodium sulfanilate is produced by the reaction between sulfanilic acid and sodium hydroxide. Suggest why sodium sulfanilate is used in the preparation of methyl orange rather than sulfanilic acid.

Sodium sulfanilate is more soluble in water than sulfanilic acid. [1]

[Turn over



(b) Nitrous acid is formed **in situ** by the reaction of sodium nitrite and hydrochloric acid.

(i) Suggest an explanation of the term **in situ**.

It is made in the reaction vessel (not added separately). [1]

(ii) Write an equation for the reaction between sodium nitrite and hydrochloric acid.

$\text{NaNO}_2 + \text{HCl} \rightarrow \text{HNO}_2 + \text{NaCl}$ [1]

(iii) Suggest why the solution was poured over crushed ice.

The diazonium ion is unstable and decomposes at temperatures above 10 °C. [1]

(c) (i) Calculate the volume of N,N-dimethylaniline added to ethanoic acid.

volume = $1.71 \div 0.956 = 1.79 \text{ cm}^3$ [1]

(ii) Suggest an equation for the reaction between N,N-dimethylaniline and ethanoic acid.

$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 + \text{CH}_3\text{COOH} \rightarrow$
 $\text{CH}_3\text{COO}^- \text{C}_6\text{H}_5\text{N}^+\text{H}(\text{CH}_3)_2$ [2]

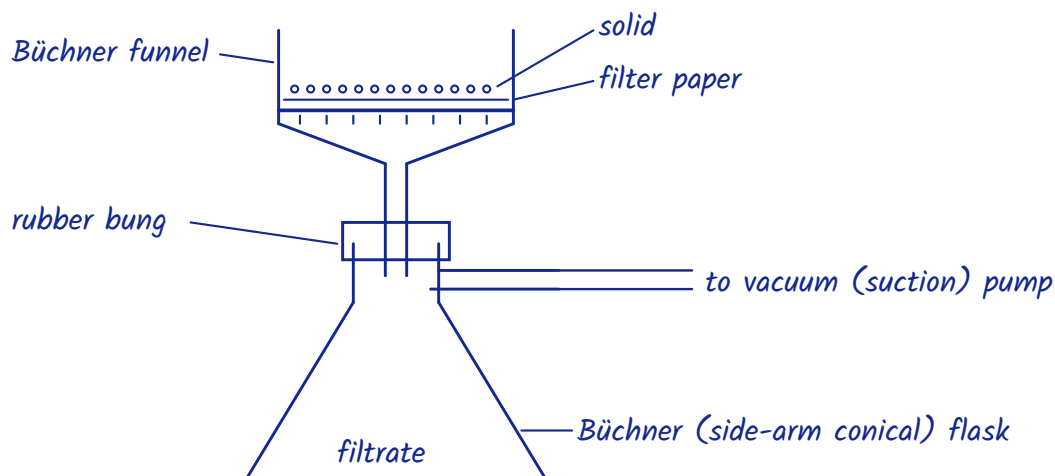


(d) State a practical use for methyl orange.

As an indicator in acid-base titrations.

[1]

(e) (i) Draw a labelled diagram to show how suction filtration is carried out.



[3]

(ii) State **two** advantages of suction filtration.

Faster than gravity filtration.

A drier product is obtained.

[2]

[Turn over]



- (f) (i) Describe how the melting point of the recrystallised methyl orange was determined.

Put some dry solid in a capillary tube sealed at one end.

Heat slowly in a melting point apparatus.

Record the temperatures at which the solid starts to melt and finishes melting.

[3]

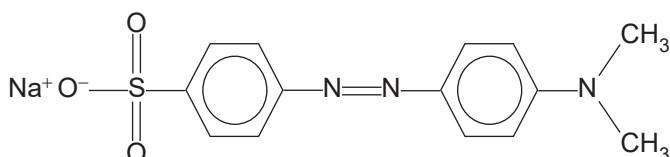
- (ii) Describe how the melting point value obtained in (f)(i) would differ from 300 °C if the sample was impure.

It would melt at a lower temperature than 300 °C.

It would melt over a larger range of temperature (not sharp).

[2]

- (g) A structure of methyl orange is given below.



- (i) Determine which reactant, sodium sulfanilate (2.70 g) or N,N-dimethylaniline (1.71 g), is the limiting reactant in this synthesis of methyl orange.

moles of sodium sulfanilate = $2.70 \div 195 = 0.0138 \text{ mol}$

moles of N,N-dimethylaniline = $1.71 \div 121 = 0.0141 \text{ mol}$

Ratio is 1 : 1, so sodium sulfanilate is the limiting reactant.

[3]

- (ii) Use your answer to (g)(i) to calculate the percentage yield of methyl orange. Give your answer to 1 decimal place.

moles of methyl orange = 0.0138 mol (1 : 1)

mass of methyl orange = $0.0138 \times 327 = 4.51 \text{ g}$

percentage yield = $2.32 \div 4.51 \times 100 = 51.4 \%$

[3]





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[Turn over



16ACH3213

- 4 The structure of a compound with the molecular formula C_4H_7ClO can be determined using modern spectroscopic techniques. The compound is **not** an acyl chloride.

(a) The mass spectrum of the compound contains peaks at $m/z = 106$ and $m/z = 108$. The base peak occurs at $m/z = 43$.

- (i) Explain the presence of the peaks at $m/z = 106$ and $m/z = 108$ and suggest why the peak at 106 has a higher relative abundance than the peak at 108.

Chlorine has two isotopes, ^{35}Cl and ^{37}Cl (M^+ at 106 and 108).

^{35}Cl has the higher abundance: ratio of 106 : 108 is 3 : 1.

[2]

- (ii) Suggest the formula of the fragment ion which gives rise to the base peak at $m/z = 43$.

CH_3CO^+

[1]

- (b) The high resolution nmr spectrum of the compound was obtained.

- (i) State the formula of a suitable solvent used in obtaining the nmr spectrum of the compound.

CCl_4 (or $CDCl_3$)

[1]

- (ii) Name the compound used as a standard in nmr spectroscopy and give **one** reason why it is used.

Tetramethylsilane (TMS), $Si(CH_3)_4$.

All its H atoms are equivalent, so it gives one signal.

[2]

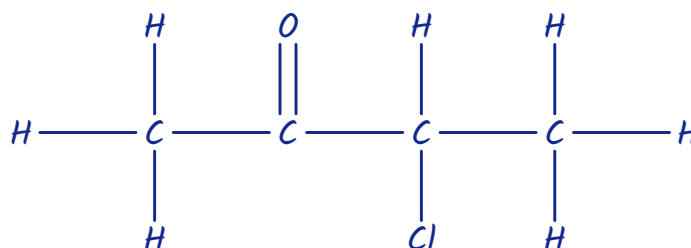


- (iii) The high resolution nmr spectrum of the compound shows three peaks. Complete the table below.

	Integration value	Splitting pattern	Number of hydrogen atoms bonded to adjacent carbon atoms
Peak 1	3	doublet	1
Peak 2	3	singlet	0
Peak 3	1	<i>quartet</i>	3

[2]

- (c) Based on your answers to (a)(ii) and (b)(iii), suggest the structure of the compound.



(3-chlorobutan-2-one, CH₃COCHClCH₃)

[1]

- (d) Describe a chemical test which could be used to show that the compound contains a carbonyl group.

Add a few drops of the compound to 2,4-dinitrophenylhydrazine

solution (Brady's reagent).

A yellow (orange) precipitate forms, showing a carbonyl group is

present.

[2]



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Question Number	Examiner Mark	Remark
1		
2		
3		
4		
Total Marks		

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General Information

1 tonne = 10^6 g

1 metre = 10^9 nm

One mole of any gas at 293 K and a pressure of 1 atmosphere (10^5 Pa) occupies a volume of 24 dm³

Avogadro Constant = 6.02×10^{23} mol⁻¹

Planck Constant = 6.63×10^{-34} Js

Specific Heat Capacity of water = $4.2 \text{ J g}^{-1} \text{ K}^{-1}$

Speed of Light = $3 \times 10^8 \text{ m s}^{-1}$



Characteristic absorptions in IR spectroscopy

Wavenumber/cm ⁻¹	Bond	Compound
550–850	C–X (X = Cl, Br, I)	Haloalkanes
750–1100	C–C	Alkanes, alkyl groups
1000–1300	C–O	Alcohols, esters, carboxylic acids
1450–1650	C=C	Arenes
1600–1700	C=C	Alkenes
1650–1800	C=O	Carboxylic acids, esters, aldehydes, ketones, amides, acyl chlorides
2200–2300	C≡N	Nitriles
2500–3200	O–H	Carboxylic acids
2750–2850	C–H	Aldehydes
2850–3000	C–H	Alkanes, alkyl groups, alkenes, arenes
3200–3600	O–H	Alcohols
3300–3500	N–H	Amines, amides

Proton Chemical Shifts in Nuclear Magnetic Resonance Spectroscopy (relative to TMS)

Chemical Shift	Structure	
0.5–2.0	–CH	Saturated alkanes
0.5–5.5	–OH	Alcohols
1.0–3.0	–NH	Amines
2.0–3.0	–CO–CH	Ketones
	–N–CH	Amines
	C ₆ H ₅ –CH	Arene (aliphatic on ring)
2.0–4.0	X–CH	X = Cl or Br (3.0–4.0) X = I (2.0–3.0)
4.5–6.0	–C=CH	Alkenes
5.5–8.5	RCONH	Amides
6.0–8.0	–C ₆ H ₅	Arenes (on ring)
9.0–10.0	–CHO	Aldehydes
10.0–12.0	–COOH	Carboxylic acids

These chemical shifts are concentration and temperature dependent and may be outside the ranges indicated above.

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Data Leaflet

Including the Periodic Table of the Elements

For the use of candidates taking
Advanced Subsidiary and
Advanced Level Examinations

Copies must be free from notes or additions of any kind. No other type of data booklet or information sheet is authorised for use in the examinations

gce a/as examinations chemistry

THE PERIODIC TABLE OF ELEMENTS																		III	IV	V	VI	VII	0	
Group																								
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18							
1 H Hydrogen 1																	4 He Helium 2							
7 Li Lithium 3	9 Be Beryllium 4											11 B Boron 5	12 C Carbon 6	14 N Nitrogen 7	16 O Oxygen 8	19 F Fluorine 9	20 Ne Neon 10							
23 Na Sodium 11	24 Mg Magnesium 12											27 Al Aluminium 13	28 Si Silicon 14	31 P Phosphorus 15	32 S Sulfur 16	35.5 Cl Chlorine 17	40 Ar Argon 18							
39 K Potassium 19	40 Ca Calcium 20	45 Sc Scandium 21	48 Ti Titanium 22	51 V Vanadium 23	52 Cr Chromium 24	55 Mn Manganese 25	56 Fe Iron 26	59 Co Cobalt 27	59 Ni Nickel 28	64 Cu Copper 29	65 Zn Zinc 30	70 Ga Gallium 31	73 Ge Germanium 32	75 As Arsenic 33	79 Se Selenium 34	80 Br Bromine 35	84 Kr Krypton 36							
85 Rb Rubidium 37	88 Sr Strontium 38	89 Y Yttrium 39	91 Zr Zirconium 40	93 Nb Niobium 41	96 Mo Molybdenum 42	98 Tc Technetium 43	101 Ru Ruthenium 44	103 Rh Rhodium 45	106 Pd Palladium 46	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54							
133 Cs Caesium 55	137 Ba Barium 56	139 La [*] Lanthanum 57	178 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	192 Ir Iridium 77	195 Pt Platinum 78	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	210 Po Polonium 84	210 At Astatine 85	222 Rn Radon 86							
223 Fr Francium 87	226 Ra Radium 88	227 Ac [†] Actinium 89	261 Rf Rutherfordium 104	262 Db Dubnium 105	266 Sg Seaborgium 106	264 Bh Bohrium 107	277 Hs Hassium 108	268 Mt Meitnerium 109	271 Ds Darmstadtium 110	272 Rg Roentgenium 111	285 Cn Copernicium 112													
			140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	145 Pm Promethium 61	150 Sm Samarium 62	152 Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	162 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71								
			232 Th Thorium 90	231 Pa Protactinium 91	238 U Uranium 92	237 Np Neptunium 93	242 Pu Plutonium 94	243 Am Americium 95	247 Cm Curium 96	245 Bk Berkelium 97	251 Cf Californium 98	254 Es Einsteinium 99	253 Fm Fermium 100	256 Md Mendelevium 101	254 No Nobelium 102	257 Lr Lawrencium 103								

a

X

b

a = relative atomic mass (approx)

x = atomic symbol

b = atomic number

* 58 – 71 Lanthanum series
† 90 – 103 Actinium series

a

X

b

a = relative atomic mass (approx)
x = atomic symbol
b = atomic number