



CHEMISTRY

2006 NATIONAL QUALIFYING EXAMINATION

Time Allowed
Reading Time: 15 minutes
Examination Time: 120 minutes

INSTRUCTIONS

- This paper is in **two** sections and you must answer each section according to the instructions.

Section A: Answer **ALL** questions — spend no more than 30 minutes on this section.
[This section is worth 30 marks.]
Section B: Apportion your time equally on the questions in this section.
Answer **ANY THREE (3)** of Questions 16, 17, 18 or 19
[This section is worth 90 marks.]
- All answers to Section A must be answered, using a 2B pencil, on the Multiple Choice answer sheet.
- All answers to Section B must be written in the space provided in the answer book.
- Use **blue** or **black** pen to write your answers; pencil is **NOT** acceptable.
- Rough working must be done only on pages 31 to 33 of this booklet.
- You are not permitted to refer to books, periodic tables or written notes.
- The only permitted aid is a non-programmable electronic calculator.
- Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant (N)	$6.02 \times 10^{23} \text{ mol}^{-1}$	Velocity of light (c)	$2.998 \times 10^8 \text{ m s}^{-1}$
1 faraday	96,486 coulombs	Density of water at 25°C	0.9971 g cm^{-3}
1 coulomb	1 A s	Acceleration due to gravity	9.81 m s^{-2}
Universal gas constant (R)		1 newton (N)	1 kg m s^{-1}
8.314 J K ⁻¹ mol ⁻¹			
$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$			
Planck's constant (h)	$6.626 \times 10^{-34} \text{ J s}$	1 pascal (Pa)	1 N m^{-1}
Standard temperature and pressure (STP)		pH = $-\log_{10}[\text{H}^+]$ pH + pOH = 14.00 at 25°C $K_a = [\text{H}^+][\text{A}^-] / [\text{HA}]$ PV = nRT E = hv c = vλ	
273 K and 101.3 kPa			
0°C and 101.3 kPa			
0°C and 1 atm			
0°C and 760 mm Hg			
Molar volume of ideal gas at STP	22.4 L	Surface area of sphere A = $4\pi r^2$	
1 atm = 101.3 kPa			

ATOMIC NUMBERS & RELATIVE ATOMIC MASSES*

1 H	1.008	23 V	50.94	45 Rh	102.9	67 Ho	164.9	89 Ac	(227)
2 He	4.003	24 Cr	52.00	46 Pd	106.4	68 Er	167.3	90 Th	232.0
3 Li	6.941	25 Mn	54.94	47 Ag	107.9	69 Tm	168.9	91 Pa	(231)
4 Be	9.012	26 Fe	55.85	48 Cd	112.4	70 Yb	173.0	92 U	238.0
5 B	10.81	27 Co	58.93	49 In	114.8	71 Lu	175.0	93 Np	(237)
6 C	12.01	28 Ni	58.69	50 Sn	118.7	72 Hf	178.5	94 Pu	(244)
7 N	14.01	29 Cu	63.55	51 Sb	121.8	73 Ta	180.9	95 Am	(243)
8 O	16.00	30 Zn	65.38	52 Te	127.6	74 W	183.9	96 Cm	(247)
9 F	19.00	31 Ga	69.72	53 I	126.9	75 Re	186.2	97 Bk	(247)
10 Ne	20.18	32 Ge	72.59	54 Xe	131.3	76 Os	190.2	98 Cf	(251)
11 Na	22.99	33 As	74.92	55 Cs	132.9	77 Ir	192.2	99 Es	(252)
12 Mg	24.31	34 Se	78.96	56 Ba	137.3	78 Pt	195.1	100Fm	(257)
13 Al	26.98	35 Br	79.90	57 La	138.9	79 Au	197.0	101Md	(258)
14 Si	28.09	36 Kr	83.80	58 Ce	140.1	80 Hg	200.6	102No	(259)
15 P	30.97	37 Rb	85.47	59 Pr	140.9	81 Tl	204.4	103Lw	(260)
16 S	32.07	38 Sr	87.62	60 Nd	144.2	82 Pb	207.2	104Db	
17 Cl	35.45	39 Y	88.91	61 Pm	(145)	83 Bi	209.0	105Jt	
18 Ar	39.95	40 Zr	91.22	62 Sm	150.4	84 Po	(209)	106Rf	
19 K	39.10	41 Nb	92.91	63 Eu	152.0	85 At	(210)	107Bh	
20 Ca	40.08	42 Mo	95.94	64 Gd	157.3	86 Rn	(222)	108Hn	
21 Sc	44.96	43 Tc	(98) [†]	65 Tb	158.9	87 Fr	(223)	109Mt	
22 Ti	47.88	44 Ru	101.1	66 Dy	162.5	88 Ra	226.0		

* The relative values given here are to four significant figures.

[†] A value given in parentheses denotes the mass of the longest-lived isotope.

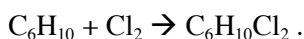
SECTION A

It is intended that candidates devote not more than **30 minutes to this section**. Answer **ALL** fifteen (15) questions in this section. Only one choice is allowed per question and this should be made by clearly crossing the chosen answer box in **the answer book**. If you make a mistake **make sure that your incorrect answer is completely erased**.

Please note the following:

- It is recommended that you first record your answer on this question paper by circling **ONE** of the letters **A, B, C, D** or **E**.
- Then transfer these answers on to the computer sheet which will be computer marked for assessment.

Q1 A student is attempting to prepare 1,2-dichlorocyclohexene according to the equation



20.0 g of C_6H_{10} was mixed with excess chlorine, and 18.3 g of $\text{C}_6\text{H}_8\text{Cl}_2$ obtained. What was the percentage yield?

- A** 45.8%
- B** 49.1%
- C** 53.7%
- D** 64.0%
- E** 91.5%

Q2 What is the oxidation number of antimony (Sb) in caesium heptafluorodiantimonate, CsSb_2F_7 ?

- A** -I
- B** 0
- C** I
- D** III
- E** V

Q3 Which of the following statements correctly describe what occurs when liquid CH_2F_2 evaporates?

- I. Dispersion forces are overcome.
- II. Dipole-dipole forces are overcome.
- III. Hydrogen bonds are broken.

- A** I only
- B** II only
- C** III only
- D** I and II only
- E** I, II and III

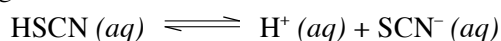
- Q4** Iodine adds to the double bonds in fatty acids (one iodine molecule per double bond). How many double bonds are in a molecule of α -linolenic acid, which has a molar mass of 278.4 g mol^{-1} , if 0.125 g of the acid requires 0.342 g of iodine for complete reaction?

A 1
B 2
C 3
D 4
E 5

- Q5** Which of these industrial processes does **not** involve oxidation or reduction?

A Formation of iron from the reaction of iron ore and carbon monoxide.
B Electrolysis of molten aluminium ore.
C Purification of zinc ore by roasting with pure oxygen.
D Treatment of gold ores with bacterial cultures to eliminate sulfides by conversion to sulfates.
E The addition of NaOH to digest aluminium oxides.

- Q6** A solution was prepared by dissolving 0.250 mol thiocyanic acid, HSCN, in 250 mL water, where the acid dissociated according to



The solution was found to have an equilibrium concentration of 0.31 mol L^{-1} of hydrogen ions. Calculate the equilibrium constant (K_a) for the above reaction.

A 0.096 mol L^{-1}
B 0.14 mol L^{-1}
C 0.31 mol L^{-1}
D 0.45 mol L^{-1}
E 1.24 mol L^{-1}

- Q7** The normal boiling points of four elements with consecutive atomic numbers are tabulated below:

	W	X	Y	Z
Atomic number	N	$N + 1$	$N + 2$	$N + 3$
Normal boiling point /°C	58	-152	688	1380

(Note that W, X, Y and Z are codes which are unrelated to the elements' real symbols.)

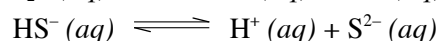
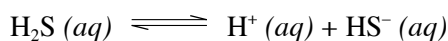
Which of the following compounds would be the most stable?

A W_2X
B W_2Y
C W_2Z
D XZ
E XY_2

- Q8** Jason hurt his ankle while playing basketball and used an ammonium nitrate cold-pack to soothe the pain. These packs consist of crystals of ammonium nitrate and liquid water; they are activated by allowing the crystals to dissolve in water, which lowers the temperature of the pack. Why does ammonium nitrate dissolve spontaneously in water?
- A** The reaction is exothermic, and thus increases the temperature (and the disorder) of the surroundings.
 - B** The dissolved particles of ammonium nitrate are more randomly ordered than the crystalline particles – which is favourable.
 - C** The reaction is endothermic, and so causes heat from the surroundings to be dispersed into the cold-pack.
 - D** The reaction is endothermic, so the solution is colder and thus at lower energy – which is favourable.
 - E** The mechanical force of punching the bag agitates the ammonium nitrate particles and dissolves them.
- Q9** One mole of an organic compound containing 5 carbon atoms per molecule burns with 7 moles of oxygen gas to give carbon dioxide and water in equimolar amounts. Which of the following functional groups could the compound **not** contain?
- A** ether
 - B** alcohol
 - C** ketone
 - D** carboxylic acid
 - E** alkene
- Q10** This year marks the centenary of Henri Moissan's receiving the Nobel Prize in Chemistry for the first laboratory production of fluorine gas. Which property of fluorine had made it so difficult to isolate?
- A** It is very volatile.
 - B** It has a low molecular mass.
 - C** It readily forms free radicals.
 - D** It is a very powerful reducing agent.
 - E** It is a very powerful oxidising agent.
- Q11** The nitrate salt of an unknown metal is dissolved in water and electrolysed. The unknown metal is deposited on the cathode, which increases in mass by 1.79 g, and 6.34 g of the copper anode dissolves into solution.
- Which one of the following is the unknown metal?
- A** Sr
 - B** Ge
 - C** Al
 - D** Na
 - E** Cu

- Q12** Considering air as a 4:1 mixture of nitrogen and oxygen, what is the density of air at 25 °C and 1 atm?
- A 1.18 mg L⁻¹
 - B 11.62 mg L⁻¹
 - C 1.18 g L⁻¹
 - D 1.29 g L⁻¹
 - E 28.8 g L⁻¹

- Q13** Hydrogen sulfide, H₂S, is a weak acid which dissociates in solution according to the following equations:



Manganese(II) sulfide, MnS, is a sparingly soluble pink solid which, when suspended in water, also exists in equilibrium with ions in solution:



In which of the following aqueous solutions would manganese(II) sulfide be most soluble?

- A 1 mol L⁻¹ HCl
 - B 1 mol L⁻¹ H₂S
 - C 1 mol L⁻¹ Mn(NO₃)₂
 - D 1 mol L⁻¹ NH₃
 - E pure water
- Q14** The output of a diesel generator, which contains a mixture of CO₂ and H₂O gases, is collected in a sealed vessel at 447 K. As the mixture cools to 298 K, the pressure falls from 3.0 atm to 0.80 atm.

What is the ratio of CO₂ to H₂O in the mixture?

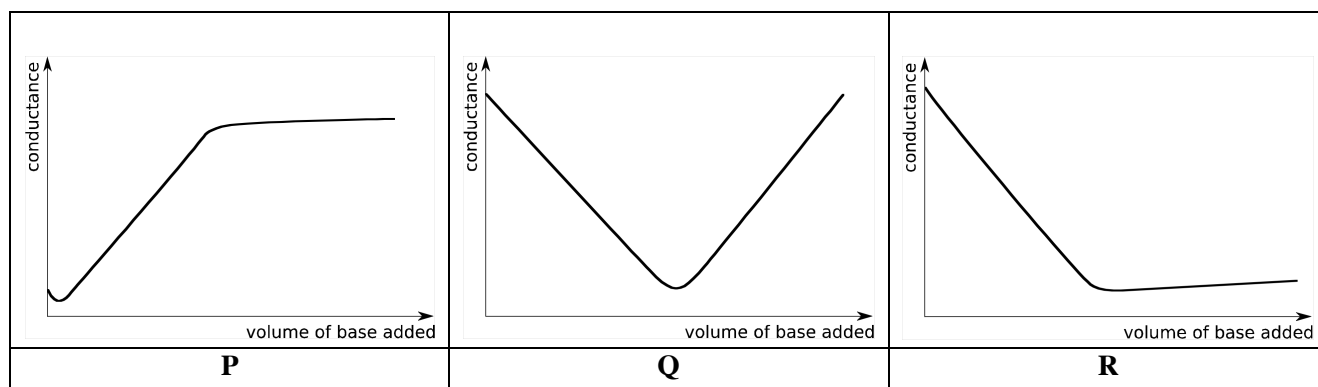
- A 2:3
- B 1:1
- C 2:5
- D 1:4
- E 1:5

Q15 Conductimetric titration is a laboratory technique in which the electrical conductance of a solution is measured over the course of a titration. These measurements are used instead of a visible indicator to determine the endpoint of the titration. Although not as widely applicable as traditional acid-base indicators, this technique can be used in some situations where the traditional method would not work.

Three conductimetric titrations were performed, as follows:

- I. Dilute acetic acid was titrated with dilute ammonia solution.
- II. Dilute nitric acid was titrated with dilute ammonia solution.
- III. Dilute nitric acid was titrated with dilute sodium hydroxide solution.

The conductance curves obtained are shown below:



Which of the following alternatives correctly matches each titration to the conductance curve it gave?

	Titration I	Titration II	Titration III
A	Q	P	R
B	R	P	Q
C	R	Q	P
D	P	Q	R
E	P	R	Q

SECTION B

Marks will be deducted for incorrect use of significant figures. You are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Answer any three of the four questions in this section.

Question 16

A clear, colourless solution of an unknown metal nitrate solution ($M(NO_3)_2$) of unknown concentration is given as a challenge to a student from her teacher. She is told that the metal is either copper (Cu), magnesium (Mg), lead (Pb) or zinc (Zn). The student remembers performing an experiment in which freshly cleaned pieces of zinc and copper were consecutively placed in solutions containing other metal ions. When zinc metal was placed in solutions containing lead or copper ions, a fine black precipitate formed on the metal surface. When it was placed in a solution containing magnesium ion, no reaction was observed. On the other hand, no change was observed when the copper metal was placed in any of the solutions containing lead, magnesium or zinc ions. After the experiment the student's teacher told her that the fine black precipitate was actually a metal in a microcrystalline state.

- (a) Using some basic chemical knowledge and the information given rank the four metals above in order of decreasing reactivity. **[2 marks]**

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Most reactive

Least reactive

- (b) Which metal is the strongest reductant (that is, has the greatest ability to reduce other species)? **[1 mark]**

- (c) Write two balanced ionic half equations and a full redox equation for the reaction between zinc metal and a solution containing lead ions. **[3 marks]**

Reduction
half equation

Oxidation
half equation

Redox equation

The student uses the information from this experiment to help her identify the unknown metal. When freshly cleaned pieces of copper and zinc are placed in the unknown solution no reaction is observed. She then adds some potassium hydroxide (KOH) solution to a sample of the unknown solution. It produces a white precipitate which dissolves when more KOH is added. She can now identify the unknown metal.

- (d) What is the unknown metal of the solution? **[1 mark]**

[note: Parts (e) to (l) can be completed without an answer to parts (a) to (d)]

To find the concentration of the solution the student decides to use an iodometric method using potassium iodide (KI) and potassium ferricyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]$). A 25.00 mL aliquot of the original unknown solution is transferred to a 500 mL conical flask containing a buffer solution and approximately 100–150 mL of distilled water. 3 g of KI and approximately 30–35 mL of a 0.1 mol L^{-1} solution of $\text{K}_3[\text{Fe}(\text{CN})_6]$ are then added. The flask is then covered and placed in a cupboard to allow these reagents to react, forming triiodide ions (I_3^-) and ferrocyanide ions ($[\text{Fe}(\text{CN})_6]^{4-}$). In fact, this equilibrium lies to the left; the reason this reaction occurs is that it is driven by the subsequent reaction of the ferrocyanide ions with the unknown metal ions (M^{2+}) and potassium ions to form solid potassium M ferrocyanide ($\text{K}_2\text{M}_3[\text{Fe}(\text{CN})_6]_2$). The triiodide formed in these reactions is then titrated with 0.100 mol L^{-1} potassium thiosulfate ($\text{K}_2\text{S}_2\text{O}_3$) to give iodide and tetrathionate ($\text{S}_4\text{O}_6^{2-}$) ions. Three titrations are performed and require an average of 23.10 mL of thiosulfate solution.

- (e) Determine the oxidation number of the following: **[4 marks]**

Fe in $\text{K}_3[\text{Fe}(\text{CN})_6]$

(hint: CN has a charge of -1)

Fe in $\text{K}_2\text{M}_3[\text{Fe}(\text{CN})_6]_2$

S in $\text{K}_2\text{S}_2\text{O}_3$

S in $\text{S}_4\text{O}_6^{2-}$

- (f) Write two balanced ionic half equations and a full redox equation for the reaction between iodide ions and ferricyanide ($[\text{Fe}(\text{CN})_6]^{3-}$) ions. **[6 marks]**

Reduction
half equation

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Oxidation
half equation

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Full equation

--

- (g) Write an equation for the formation of solid potassium M ferrocyanide, ($\text{K}_2\text{M}_3[\text{Fe}(\text{CN})_6]_2$). **[2 marks]**

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- (h) For every M^{2+} ion, how many triiodide ions are produced? **[1 mark]**

- (i) Write two balanced ionic half equations and a full redox equation for the reaction between triiodide ions and thiosulfate ions. **[4 marks]**

Reduction
half equation

Oxidation
half equation

Full equation

- (j) For every M^{2+} ion, how many thiosulfate ions are required? **[1 mark]**

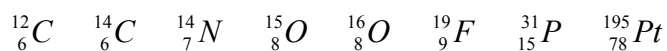
- (k) What is the original concentration of the unknown solution? **[2 marks]**

The student confidently shows her teacher the answer, only to be told that the titration reaction that she performed does not occur to completion. The reaction between the unknown metal and ferrocyanide ions only reaches 99.3% completion; moreover, the end point occurs prematurely, when only 99.4% of the triiodide has reacted. As these correction values are consistent for this titration, the true value for the concentration can be obtained.

- (1) What is the true concentration of the unknown solution? **[3 marks]**

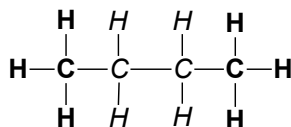
Question 17

Nuclear Magnetic Resonance (NMR) Spectroscopy is a technique which is used to determine the structure of chemical compounds, especially of organic compounds. It can be used to give information about any isotope of an atom, **unless the isotope has both an even number of protons and an even number of neutrons**. From the following list, circle the isotopes which **can** be studied by NMR spectroscopy. [2 marks]



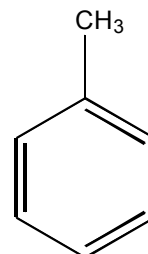
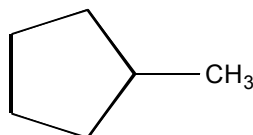
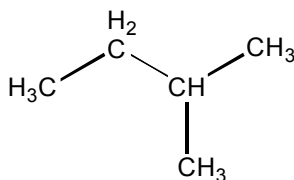
NMR spectroscopy involves placing a compound in a magnetic field and measuring the interaction between the nuclei of the atoms and that magnetic field. By selecting magnetic fields of different strengths, different types of nuclei can be studied separately. The two most common forms of NMR spectroscopy are ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectroscopy, which give information about hydrogen and carbon atoms, respectively. There are a number of pieces of information in an NMR spectrum which can allow us to piece together the structure of the compound, one of which is the number of signals in the NMR spectrum.

The number of signals tells us how many different “types” of a particular nucleus are present in a molecule. Nuclei are considered to be identical (of the same “type”) if they are connected to identical sequences of atoms. For example, the symmetrical molecule C_4H_{10} below contains 2 “types” of carbon atoms and 2 “types” of hydrogen atoms (distinguished in bold and italics) as the molecule is symmetrical, and hydrogens attached to the same carbon are identical in this case.



The ${}^1\text{H}$ and ${}^{13}\text{C}$ NMR spectra for this compound will therefore each contain two signals.

- (a) How many signals would the (i) ${}^1\text{H}$ and (ii) ${}^{13}\text{C}$ NMR spectra of the following compounds contain? [3 marks]



(i) ${}^1\text{H}$			
(ii) ${}^{13}\text{C}$			

NMR spectra can be used to distinguish between isomers of compounds. Structural isomers are compounds with the same molecular formulae, but different arrangement of atoms and bonds.

- (b) Draw the three structural isomers of C_3H_{12} . [3 marks]

(I)	(II)	(III)

- (c) For each of the compounds you drew above, how many signals would you expect to appear in a ^1H NMR spectrum? In a ^{13}C NMR spectrum? [**3 marks**]

(I) ^1H NMR: ^{13}C NMR:	(II) ^1H NMR: ^{13}C NMR:	(III) ^1H NMR: ^{13}C NMR:
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Often, the information found in NMR spectra is combined with the information from other forms of spectroscopy to elucidate an unknown structure. An unknown organic compound was subjected to elemental analysis and found to contain 83.6% C and 16.4% H.

- (d) What is the empirical formula for this compound? Show your working. [**2 marks**]

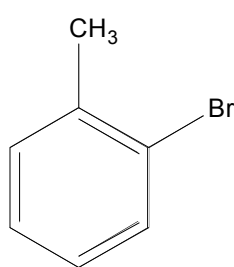
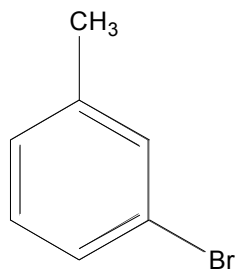
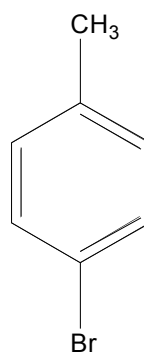
Mass spectrometry was then performed, and revealed that the compound had a molecular mass of 86.2 g mol^{-1} .

- (e) What is the molecular formula of the compound? Show your working. [**1 mark**]

^1H and ^{13}C NMR spectroscopy is then performed on the compound. In each spectrum there are only 2 signals.

- (f) Draw the structure of the unknown compound. [**2 marks**]

NMR is also useful in distinguishing between the isomers of aromatic compounds. When more than one substituent is attached to benzene, a number of isomers are possible. These isomers are named according to the relative positions of the two substituents.

*ortho**meta**para*

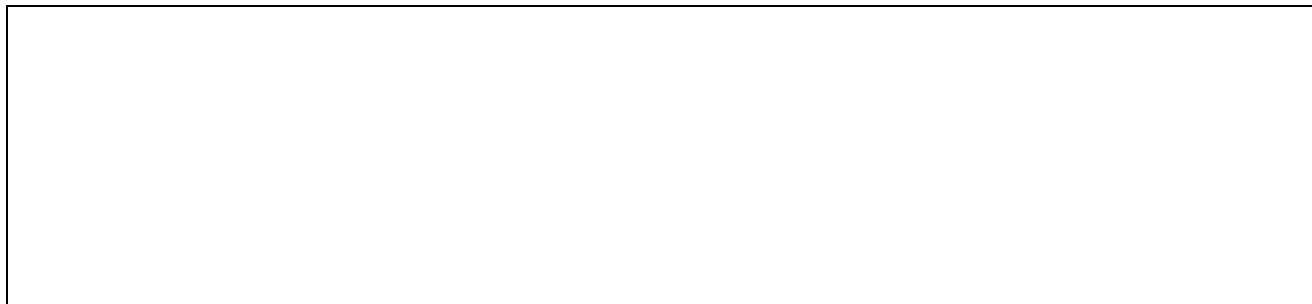
The *ortho* isomer shown above has 5 signals in its ^1H NMR spectrum and 7 signals in its ^{13}C NMR spectrum.

(g) How many ^1H and ^{13}C signals would you expect for the *meta* and *para* isomers? [2 marks]

<i>meta</i> ^1H NMR: ^{13}C NMR:	<i>para</i> ^1H NMR: ^{13}C NMR:
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A chemist has synthesised a compound and found that it has molecular formula $\text{C}_6\text{H}_4\text{Br}_2$. He knows that it is an aromatic compound (i.e. contains a benzene ring). In order to determine its structure, he obtained a ^1H NMR spectrum, and found that it contained three peaks.

(h) Draw the structure of the compound which he synthesised. [2 marks]

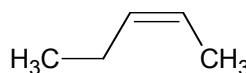
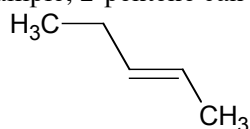


To confirm his structure, he also plans to obtain a ^{13}C NMR spectrum.

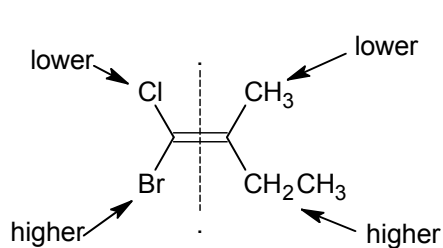
(i) How many peaks should he observe? [1 mark]



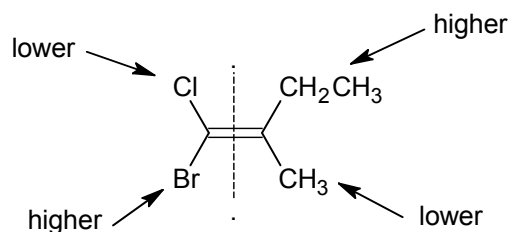
In addition to the structural isomers we have examined above, there are a number of other forms of isomers. One group, geometric isomers, describes compounds which have the same molecular formula, and the same atom sequence, but different spatial arrangements. Compounds containing a double bond can exhibit geometric isomerism. For example, 2-pentene can exist as either of the following isomers:



The two geometric isomers are designated (*E*) or (*Z*), depending upon the arrangement of the groups about the double bond. The assignment is made by firstly drawing a line perpendicular to the double bond, as shown below. Then, compare the two groups attached to the carbon on each side of the double bond, labelling one as higher and the other as lower priority. An atom is given higher priority if it has a higher atomic number. If both atoms are identical, evaluate the next atom in the chain. The isomer which has both “lower” designations on the same side of the double bond is called (*Z*), and the group in which the two “lower” designations are on opposite sides is called (*E*), as shown below.

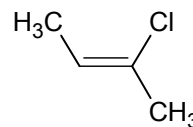
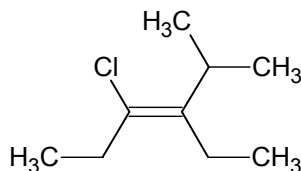
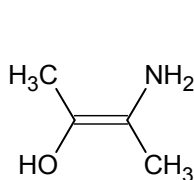


(Z)



(E)

- (j) Indicate whether the following compounds have an (*E*) or a (*Z*) configuration. [1.5 marks]



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More than two isomers are possible for compounds with two or more double bonds.

- (k) Draw all the possible isomers of 2,4-hexadiene, indicating whether each double bond is (*E*) or (*Z*). [4.5 marks]

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One of the isomers of 2,4-hexadiene was analysed by ^1H NMR spectroscopy and the resulting spectrum found to contain six peaks.

(l) Draw this isomer. [**3 marks**]

Question 18

Covalent bonds, even between the same two atoms, can have a wide range of lengths and strengths. For instance, consider the three molecules nitrogen gas (N_2), dinitrogen tetrafluoride (N_2F_4), and difluorodiazene (N_2F_2), each of which contains a covalent bond between two nitrogen atoms.

- (a) Draw Lewis structures (electron dot diagrams) for each of these molecules. (You should show all valence electrons, either as a dot (or circle or cross) or using a line to represent a pair of electrons.)

[3 marks]

N_2	N_2F_4	N_2F_2

- (b) Arrange these molecules in order of increasing N—N bond length. **[1 mark]**

shortest bond length		greatest bond length

- (c) Arrange these molecules in order of increasing N—N bond strength. (Increased strength means that more energy is needed to break the bond.) **[1 mark]**

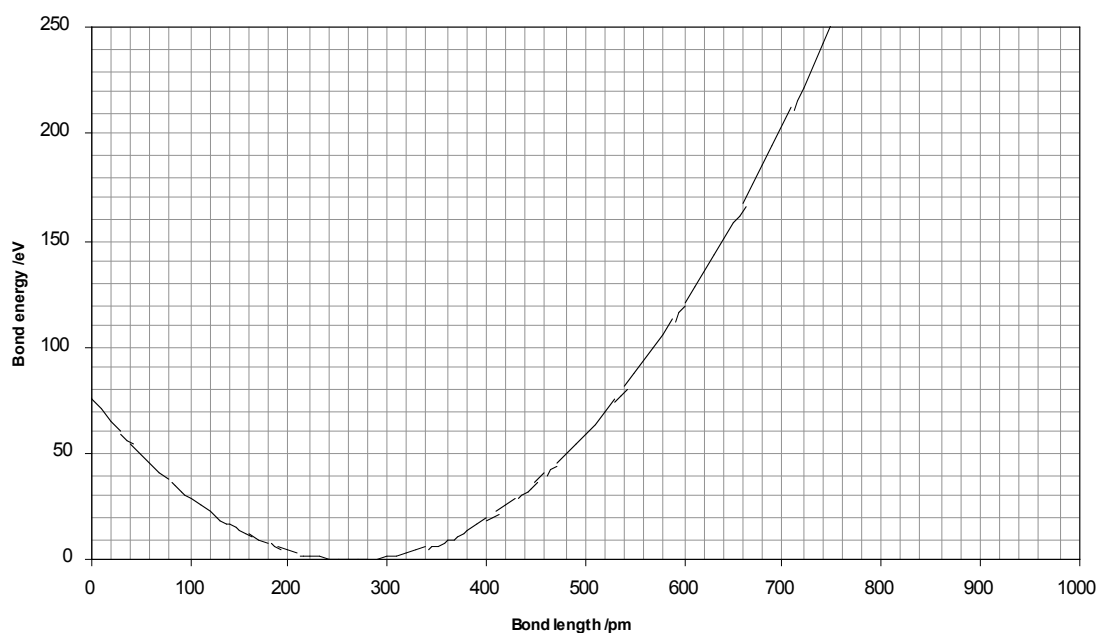
weakest bond		strongest bond

If enough energy is added to a covalent bond, the bond will break. As an example, iodine gas, I_2 , has a bond strength of 151 kJ mol^{-1} .

- (d) Calculate the energy needed to break the bond of a single I_2 molecule. Give your answer in electron volts (eV), where $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$. [2 marks]

If a smaller amount of energy than this is added, the bond will begin to vibrate: that is, the atoms will move back and forth so that the bond length varies. The simplest way of thinking about this is to imagine the atoms as balls connected by a spring: in this case, the energy of the bond will vary with bond length as shown in the graph below.

Bond energy against bond length of iodine gas



We can see that the equilibrium bond length of I_2 is 266 pm (where pm stands for “picometre”, and $1 \text{ pm} = 10^{-12} \text{ m}$). However, if we add 10 eV of vibrational energy, this model predicts that the bond length will oscillate back and forth between about 170 and 360 pm.

- (e) How will the bond length vary in an I_2 molecule with 30 eV of vibrational energy? [1 mark].

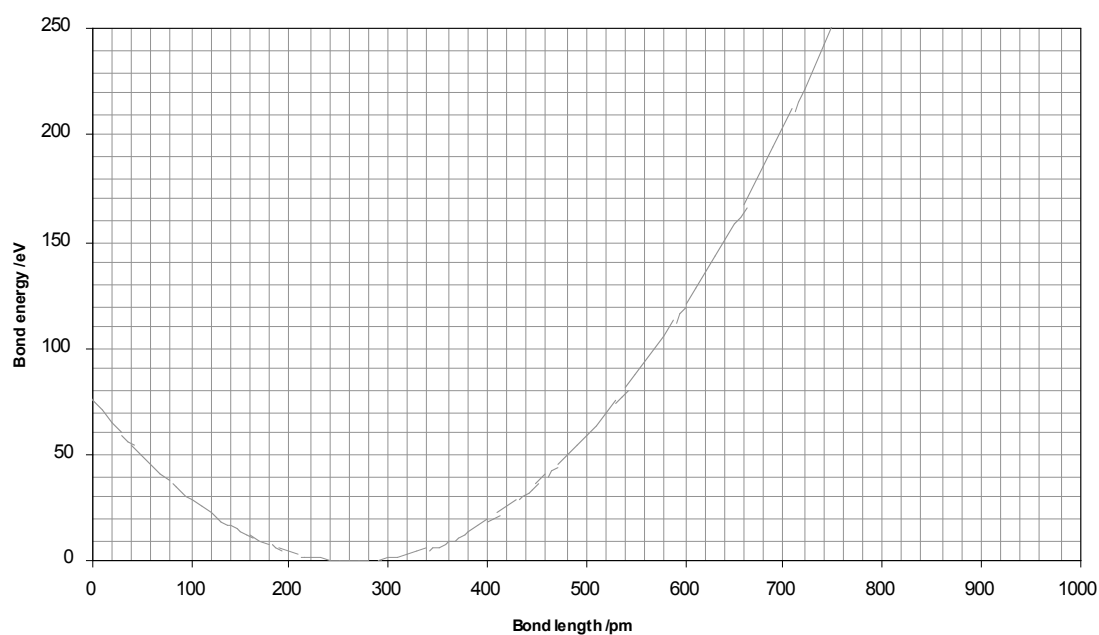
This simple model works well for small amounts of vibrational energy, but the real energy-bond length curve is more complicated.

(f) Explain briefly why this curve is inaccurate at very low bond lengths. [2 marks]

(g) Explain briefly why this curve is inaccurate at very high bond lengths. [2 marks]

(h) Keeping in mind your answers to (d), (f) and (g), draw a more realistic curve on the diagram below. [3 marks]

Bond energy against bond length of iodine gas



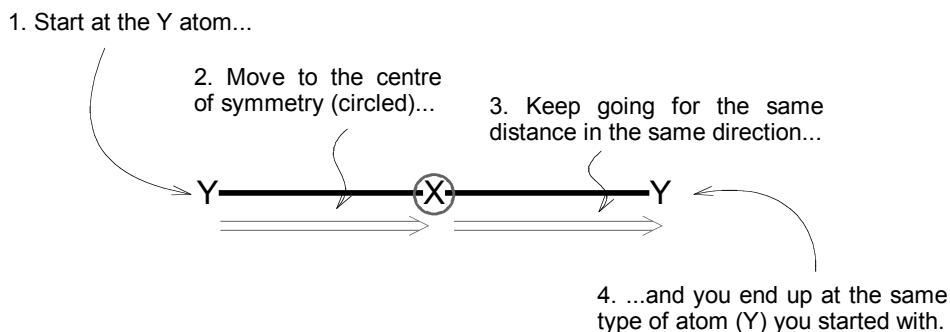
There is another problem with this simple model: the rules of quantum theory predict that molecules cannot absorb any amount of vibrational energy, but in fact absorb only quanta ("lumps") of energy of sizes which are characteristic of particular compounds. Thus if we shine infrared radiation on a compound at a range of frequencies (and hence a range of energies), we will find that only certain wavelengths are absorbed.

Chemists use two different techniques, called infrared absorption spectroscopy (IR for short) and infrared Raman spectroscopy (Raman for short), to determine the characteristic vibrational energies of a compound. According to quantum theory, these techniques obey slightly different rules and so may show different absorption wavelengths for the same compound. By comparing the IR and Raman spectra of a compound, we can find out a lot of information about its structure.

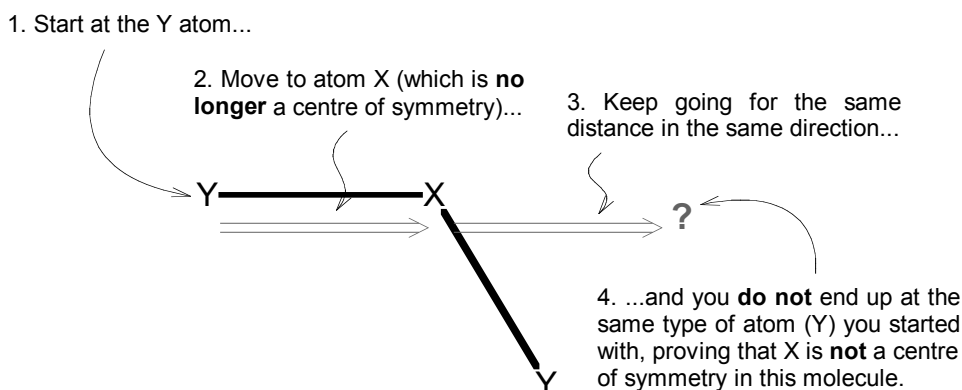
One piece of information which is particularly easy to determine is whether or not the molecule has a *centre of symmetry*. This is a special point in the molecule which has the property that:

if you **start at any atom in the molecule**
and **move to the centre of symmetry**
then **keep going for the same distance in the same direction**
you will end up at **the same type of atom you started with.**

This sounds a lot more complicated than it really is! The diagram below demonstrates the fact that a linear XY_2 molecule (such as CO_2) has a centre of symmetry on the X atom: if you follow the procedure above starting at either Y atom, you end up at the other one, and if you start at the X atom you simply stay there.



However, a bent XY_2 molecule has no centre of symmetry. The diagram below shows what happens if we try to put one on the X atom, as in the linear case: starting at a Y atom and following the procedure above, we end up at a point where there's no atom at all.



Remember that if the molecule really has a centre of symmetry, this procedure has to work for **every atom** in the molecule.

- (i) Consider each of the following geometries. If there is a centre of symmetry (COS), circle it. (You do not need to add arrows as in the diagrams above – they're just to help you understand what a centre of symmetry is.) If there is no centre of symmetry, tick the box marked "no COS". (A wedge-shaped bond is meant to be imagined coming towards you, out of the page, and a dashed bond is meant to be going away from you, into the page.) [4 marks]

trigonal planar	square planar	tetrahedral	octahedral
circle the COS OR ☐ No COS	circle the COS OR ☐ No COS	circle the COS OR ☐ No COS	circle the COS OR ☐ No COS

The reason it is so important to know whether or not a molecule has a centre of symmetry is the *rule of mutual exclusion*:

Rule of mutual exclusion: a molecule can only absorb the same frequency of radiation in its IR and Raman spectra if the molecule **does not** have a centre of symmetry.

So comparing the Raman and IR spectra of a compound may enable us to distinguish between two possible geometries. For instance, consider the following simplified summary of the strongest absorption frequencies in the spectra of gaseous titanium(II) fluoride, TiF_2 :

IR (cm^{-1})	180, 665, 766
Raman (cm^{-1})	180, 665, 766

(This means that, in both IR and Raman experiments, TiF_2 only absorbs radiation of frequencies 180, 665, and 766 cm^{-1} .)

- (j) There are two possible geometries for TiF_2 : linear and bent. Use the rule of mutual exclusion and the IR and Raman spectra to decide whether TiF_2 is linear or bent. Explain your reasoning briefly.

[2 marks]

Similarly, consider the following spectra of xenon tetrafluoride, XeF_4 :

IR (cm^{-1})	213.2, 558
Raman (cm^{-1})	515

(k) Is XeF_4 more likely to be square planar or tetrahedral? Can we tell for sure from these data?

[2 marks]

Let's reconsider difluorodiazene, N_2F_2 , which we examined at the very start of this problem. In fact, there are three possible isomers with this formula.

(l) Draw the shapes of the three isomers with formula N_2F_2 . [3 marks]

A compound of formula N_2F_2 was found to have the following spectra:

IR (cm^{-1})	363.5, 423, 990, 1437, 1581, 1993
Raman (cm^{-1})	600, 1010, 1522

(m) Which isomer of those you drew in (k) is this compound most likely to be? Why? [2 marks]

The rule of mutual exclusion is always true, but in some cases it can appear not to work. For instance, dinitrogen monoxide, N_2O , is experimentally known to be linear, but has several absorption frequencies in common between its IR and Raman spectra.

IR (cm^{-1})	588.7, 1284.9, 2223.8
Raman (cm^{-1})	588.7, 1284.9, 2223.8

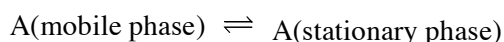
(n) Explain briefly how this is possible. **[2 marks]**

Question 19

Few methods of analysis are truly specific to a particular analyte (the compound to be analysed). It is often found that the analyte of interest must be separated from the myriad of individual compounds that may be present in a sample. As well as providing the analytical chemist with methods of separation, chromatographic techniques can also provide methods of qualitative and quantitative analysis.

Chromatography involves a sample being dissolved in a mobile phase (which may be a gas, liquid or supercritical fluid). The mobile phase is then passed through an immiscible stationary phase, which is packed into a column. The phases are chosen such that components of the sample have different affinities for each phase. A component which is strongly attracted to the stationary phase will take longer to travel through than a component which is not strongly attracted to the stationary phase, especially if it has a strong affinity for the mobile phase. As a result of these differences, sample components will become separated from each other as they travel through the stationary phase.

All chromatographic separations are based on differences in the extent to which solutes are distributed between the mobile and stationary phases. For the solute species A, the equilibrium involved is described by the equation:



The equilibrium constant, K_c , for this reaction is called the **distribution constant**, which is defined as:

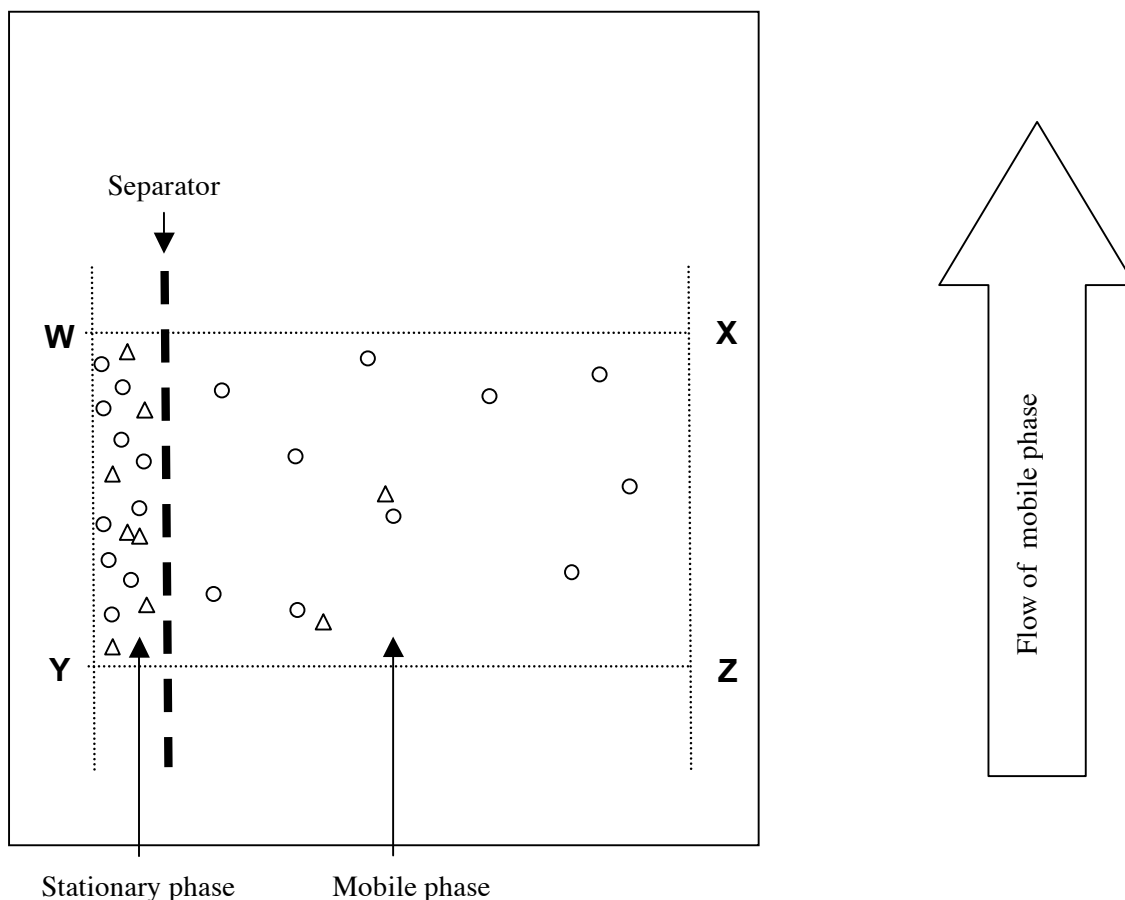
$$K_c = \frac{[A]_{\text{Stationary phase}}}{[A]_{\text{Mobile phase}}}$$

where $[A]_{\text{Stationary phase}}$ is the concentration of solute A in the stationary phase and $[A]_{\text{Mobile phase}}$ is the concentration of solute A in the mobile phase.

Ideally the distribution constant is constant over a wide range of solute concentrations.

- (a) Briefly explain how a solute will behave in a chromatographic separation if its K_c is large.
[2 marks]

- (b) Rectangle WXYZ in the diagram below represents a small segment of a chromatographic separation. Within the rectangle, the volume of the stationary phase is $5 \times 10^4 \text{ nm}^3$ and that of the mobile phase is $2 \times 10^6 \text{ nm}^3$. Each symbol $\circ$ represents a molecule of analyte A and each symbol Δ represents a molecule of analyte B. Calculate the distribution constant, K_c , for each of the analytes A and B. [2 marks]



The time between sample injection and an analyte peak reaching the detector at the end of the column is termed the **retention time**, t_R . Each analyte in the sample will have a different retention time from the others. The time taken for the mobile phase to pass through the column is called the **dead time**, t_M . The analyte is retained because it spends a time t_S in the stationary phase. Retention time is then defined as:

$$t_R = t_M + t_S$$

This is illustrated in Figure 1.

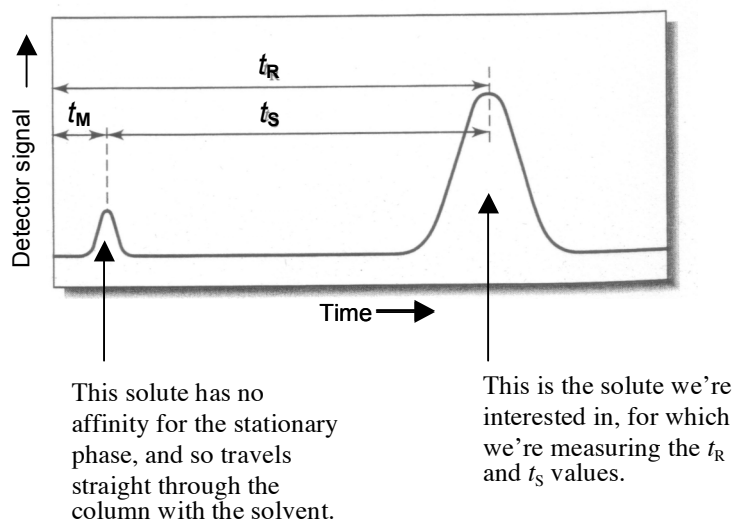


Figure 1. A typical chromatogram for a two-component mixture.

The **retention factor, k** is an important experimental parameter that is used to compare the migration rates of solutes on columns. For a given solute A, the retention factor, k_A , is defined as the amount of time solute A spends in the stationary phase relative to the time it spends in the mobile phase.

$$k_A = \frac{t_R - t_M}{t_M}$$

(c) What does it mean if a solute has a retention factor close to one? [2 marks]

Ideally separations are performed using conditions in which retention factors for the solutes in a mixture are between 1 and 5.

Two English researchers (Martin and Synge) invented the **theoretical plate model** of chromatography. They treated a chromatography column as if it were made up of discrete layers, called theoretical plates, with each layer being a new equilibrium between the stationary and mobile phases. The analyte moves along the column with the mobile phase, reaching equilibrium at each plate. This is just a MODEL – in reality there are no such things as plates inside a chromatographic column.

Two related terms widely used as quantitative measures of chromatographic column efficiency are the **plate height (H)** and **number of theoretical plates (N)**. The two are related by the following equation:

$$H = \frac{L}{N}$$

where L is the column length (usually in centimetres) of the column packing. The more theoretical plates there are present (the larger the value of N), the greater the separation between different species. Making the column longer will increase the number of theoretical plates and therefore increase the efficiency of the separation. If the column is made longer, however, analyte peaks will become broader and retention times will increase. A good way to talk about column efficiency is to use the plate height. The smaller the plate height, the more plates in a given length of column and hence the better the column efficiency.

It can be shown that the number of theoretical plates can be calculated by the following relationship:

$$N = 16 \left(\frac{t_R}{W} \right)^2$$

where W is the base width of the analyte peak. See Figure 2 for details.

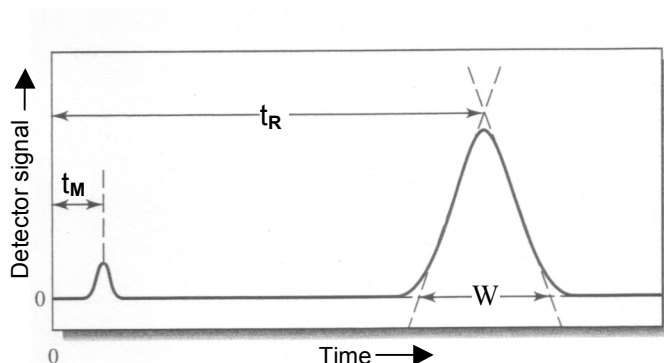


Figure 2. Determination of the number of theoretical plates, N

A further measure of how well species have been separated is provided by measurement of the **column resolution**, R_s . The resolution of two species A and B is defined by:

$$R_s = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$

A resolution of 1.5 gives an essentially complete separation of solutes A and B.

A useful equation that relates the resolution of a column to the number of theoretical plates it contains and the retention factor of a pair of solutes, A and B, on the column is:

$$R_s = \left(\frac{\sqrt{N}}{4} \right) \left(\frac{k_b}{1 + k_b} \right)$$

where k_b is the retention factor of the slower moving species.

Using this background information, answer the following questions.

Substances A and B have retention times of 16.40 and 17.63 min, respectively, on a 30.0 cm column. An unretained species passes through the column in 1.50 min. The base peak widths for A and B are 1.11 and 1.21 min, respectively.

- (d) Calculate the column resolution. **[2 marks]**

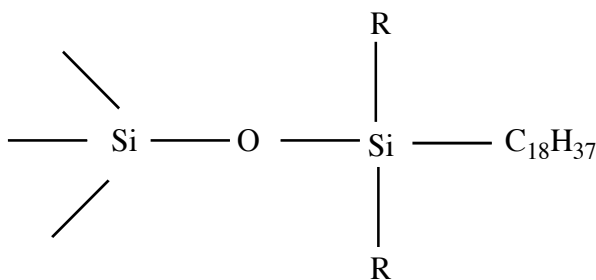
- (e) Calculate the average number of theoretical plates in the column. **[4 marks]**

- (f) Calculate the plate height. [2 marks]

- (g) Calculate the length of column required to achieve a resolution of 1.5. Assume that the retention factor does not change significantly with increasing N and L . [6 marks]

High Performance Liquid Chromatography (HPLC) is a modern technique which has become an indispensable analytical tool. The crime labs in forensic and police dramas on TV, such as CSI, often use HPLC in processing evidence. In HPLC the mobile phase is a liquid and the stationary phase can be a liquid or a solid. High performance pumps are required because of the need to achieve constant flow rates against the high back pressures developed as a result of the small particle size of the stationary phase.

A non-polar hydrocarbon (e.g., $C_{18}H_{38}$) can be chemically bonded to silica *via* a siloxane ($-\text{Si}-\text{O}-\text{Si}-$) bond. This combination can be used as a stationary phase together with a polar mobile phase (e.g., a methanol/water mixture) in a technique called **reverse-phase** chromatography. Reverse-phase chromatography is the most widely used HPLC mode. The diagram below illustrates an octadecylsilyl chemically-bonded stationary phase.

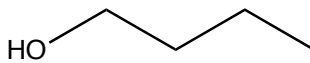


- (h) Suggest a reason why the octadecylsilyl group must be chemically bonded to the silica support. [2 marks]

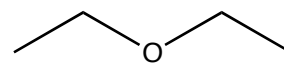
- (i) Indicate the order in which the following compounds would be eluted from an HPLC column when performing reverse-phase chromatography. [2 marks]



hexane



butan-1-ol

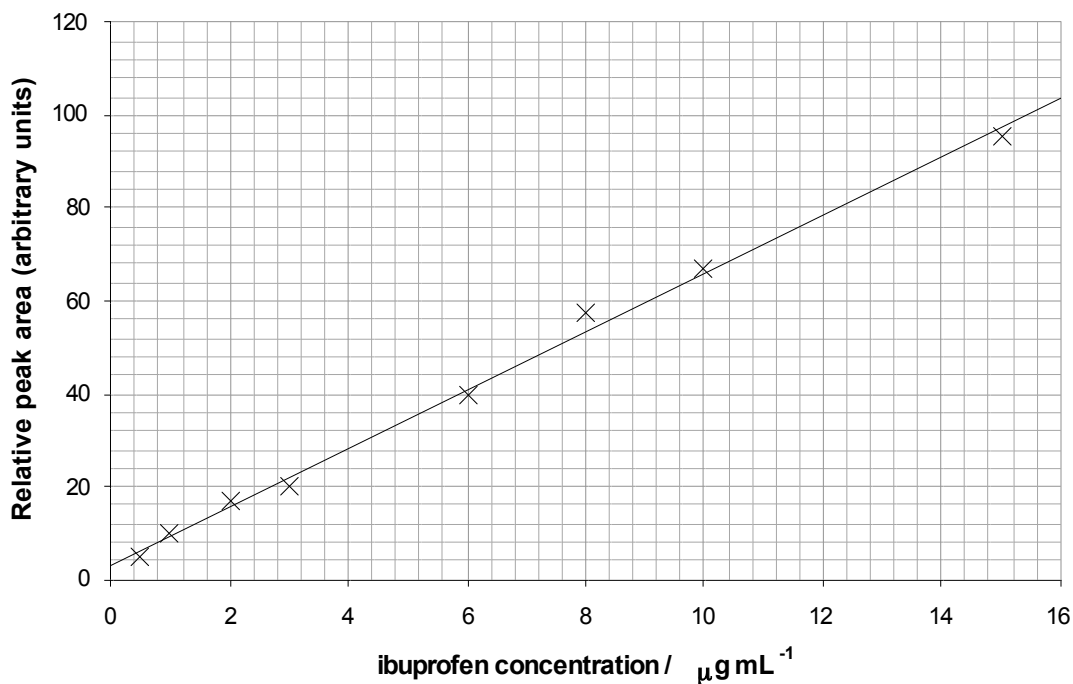


diethyl ether

Eluted first**Eluted last**

Quantitative HPLC is based on the comparison of either the height or the area of an analyte peak with that of one or more standards. If conditions are correctly controlled both peak height and peak area vary linearly with concentration. Most chromatographic instruments are equipped with computers that provide measurements of relative peak areas. The most direct method of quantitative HPLC involves the preparation of a series of standard solutions that approximate the composition of the unknown. A chromatogram for the standards is obtained and peak areas are plotted as a function of concentration to obtain a calibration curve.

An HPLC method was developed for the separation and determination of the anti-inflammatory drug ibuprofen in rat plasma samples as part of a study of the time course of the drug in laboratory animals. Several standards were subjected to HPLC and the results obtained are summarised in the following graph:

Calibration curve for detection of ibuprofen using HPLC

Next, a 10 mg kg⁻¹ sample of ibuprofen was administered orally to a laboratory rat. Blood samples were taken at various times after administration of the drug and subjected to HPLC analysis. The results obtained are summarised below.

- (j) Calculate the concentration of ibuprofen in the blood plasma for each of the times given in the above table. Complete the third column in the table below. **[4 marks]**

Time (hour)	Peak Area	Ibuprofen Concentration ($\mu\text{g mL}^{-1}$)
0	0	
0.5	91.3	
1.0	80.2	
1.5	52.1	
2.0	38.5	
3.0	24.2	
4.0	21.2	
6.0	18.5	
8.0	15.2	

- (k) During which half-hour period (1st, 2nd, 3rd, etc) is most of the ibuprofen metabolised?
[2 marks]

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