Topics in the November 2009 Exam Paper for CHEM1102
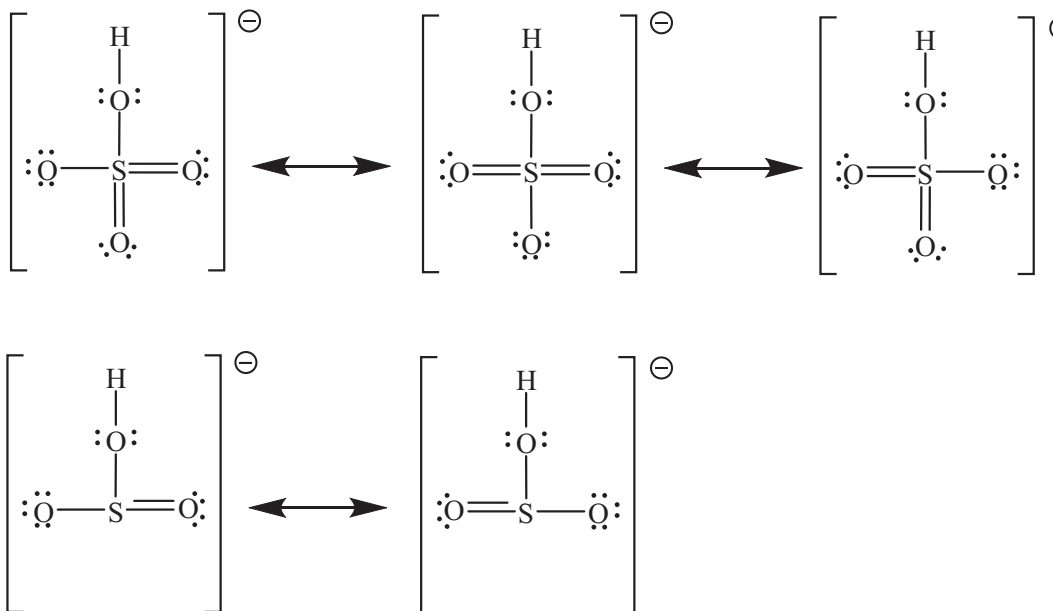
Click on the links for resources on each topic.

Marks
2

- Explain why H_2SO_4 is a stronger acid than H_2SO_3.

The acidity of oxo-acids increases as the number of oxygen atoms increases.

This is best understood in terms of the relative stability of the negative charge on the conjugate base, HSO_4^- and HSO_3^-:

The negative charge in HSO_4^- is delocalized over 3 oxygen atoms whereas that in HSO_3^- is delocalized over only 2 oxygen atoms. The greater stability of the HSO_4^- anion leads to the higher acidity of the conjugate acid, HSO_4.

- Explain why compounds of *d*-block elements are frequently paramagnetic. Use examples in your answer.

2

Paramagnetism is the property of a compound to be attracted by an external magnetic field. It is a characteristic of any compound with unpaired electrons. *d*-Block elements have from 1 to 10 electrons in the *d*-orbitals. When forming compounds, some of these may be lost to give paramagnetic species. Species with odd numbers of electrons must be paramagnetic, species with even numbers of *d*-electrons, may or may not be paramagnetic. eg

|						
Cu^{2+}, d^9	↑↓	↑↓	↑↓	↑↓	↑	must be paramagnetic
Zn^{2+}, d^{10}	↑↓	↑↓	↑↓	↑↓	↑↓	must be diamagnetic
Fe^{2+}, d^6	↑↓	↑	↑	↑	↑	is paramagnetic

ANSWER CONTINUES ON THE NEXT PAGE

- Provide a systematic name for *cis*-[Co(en)$_2$Cl$_2$]Cl. Is this complex chiral? Explain your reasoning by drawing the structure of the complex.
  en = NH$_2$CH$_2$CH$_2$NH$_2$ = ethane-1,2-diamine = ethylenediamine

3

> ***cis*-dichloridobis(ethylenediamine)cobalt(III) chloride   or**
> ***cis*-dichloridobis(ethane-1,2-diamine)cobalt(III) chloride**
>
> **The complex is chiral as it is not superimposable on its mirror image.**
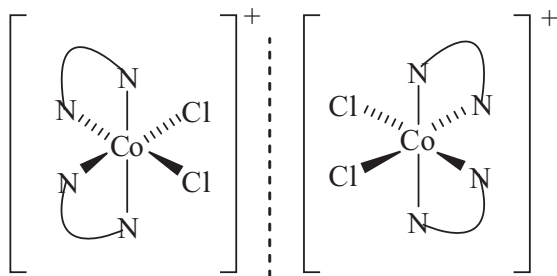
- Solution A consists of a 0.020 M aqueous solution of aspirin (acetylsalicylic acid, $C_9H_8O_4$) at 25 °C. Calculate the pH of Solution A. The pK_a of aspirin is 3.52.

As $C_9H_8O_4$ is a weak acid, $[H^+]$ must be calculated by considering the equilibrium:

	$C_9H_8O_4$	$\rightleftharpoons$	$C_9H_7O_4^-$	H^+
initial	0.020		0	0
change	$-x$		$+x$	$+x$
final	$0.020 - x$		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[C_9H_7O_4^-][H^+]}{[C_9H_7O_{24}]} = \frac{x^2}{(0.020-x)}$$

As $pK_a = 3.52$, $K_a = 10^{-3.52}$. K_a is very small so $0.020 - x \sim 0.020$ and hence:

$$x^2 = 0.020 \times 10^{-3.52} \quad \text{or} \quad x = 0.00246 \text{ M} = [H^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H^+] = -\log_{10}[0.00246] = 2.61$$

Answer: **2.61**

At 25 °C, 1.00 L of Solution B consists of 4.04 g of sodium acetylsalicylate ($NaC_9H_7O_4$) dissolved in water. Calculate the pH of Solution B.

The molar mass of $NaC_9H_7O_4$ is:

molar mass = (22.99 (Na) + 9×12.01 (C) + 7×1.008 (H) + 4×16.00 (O)) g mol^{-1}
            = 202.136 g mol-1

Thus, 4.04 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{4.04 \text{ g}}{202.136 \text{ g mol}^{-1}} = 0.0200 \text{ mol}$$

If this is dissolved in 1.0 L, $[C_9H_7O_4^-]_{initial} = 0.0200$ M.

As $C_9H_7O_4^-$ is a weak base, $[C_9H_7O_4^-]$ must be calculated by considering the equilibrium:

ANSWER CONTINUES ON THE NEXT PAGE

	C$_9$H$_7$O$_4^-$	H$_2$O	$\rightleftharpoons$	C$_9$H$_8$O$_4$	OH$^-$
initial	0.0200	large		0	0
change	-y	negligible		+y	+y
final	0.0200 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[C_9H_8O_4][OH^-]}{[C_9H_7O_4{}^-]} = \frac{y^2}{(0.0200-y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 – 3.52 = 10.48$

As pK_b = 10.48, K_b = 10$^-$10.48. K_b is very small so 0.0200 – y ~ 0.0200 and hence:

$y^2 = 0.0200 \times 10^{-10.48}$ or $y = 0.000000814$ M = [OH$^-$]

Hence, the pOH is given by:

pOH = -$\log_{10}$[OH$^-$] = $\log_{10}$[0.000000814] = 6.09

Finally, pH + pOH = 14.00 so
pH = 14.00 – 6.09 = 7.91

Answer: **7.91**

Solution B (200.0 mL) is mixed with Solution A (400.0 mL) and water (200.0 mL) to give Solution C. Calculate the pH of Solution C after equilibration at 25 °C.

400.0 mL of solution A (the acid) contains:

number of moles = concentration × volume = (0.0200 mol L^{-1}) × (0.4000 L)
= 0.00800 mol

200.0 mL of solution B (the base) contains:

number of moles = concentration × volume = (0.0200 mol L^{-1}) × (0.2000 L)
= 0.00400 mol

The final solution has a total volume of (200.0 + 400.0 + 200.0) mL = 800.0 mL.

The concentrations of acid and base in the final solution are:

ANSWER CONTINUES ON THE NEXT PAGE

$$\text{concentration of acid} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.00800 \text{ mol}}{0.8000 \text{ L}} = 0.0100 \text{ M}$$

$$\text{concentration of base} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.00400 \text{ mol}}{0.8000 \text{ L}} = 0.00500 \text{ M}$$

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} = 3.52 + \log\frac{0.00500}{0.0100} = 3.22$$
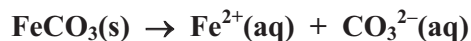
Answer: **3.22**

If you wanted to adjust the pH of Solution C to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

To lower the pH, more acid is required: solution A

	Marks
• Write a balanced chemical equation representing the dissolution of $FeCO_3$ in water at pH 7.	**4**

$$FeCO_3(s) \rightarrow Fe^{2+}(aq) + CO_3^{2-}(aq)$$

Ignoring any hydrolysis of the ions, calculate the solubility (in g L^{-1}) of $FeCO_3$ in water at pH 7. The solubility product constant, K_{sp}, for $FeCO_3$ is 2.1×10^{-11}.

From the equation above, $K_{sp} = [Fe^{2+}(aq)][CO_3^{2-}(aq)]$. If s mol of $FeCO_3$ dissolves in 1.0 L, $[Fe^{2+}(aq)] = [CO_3^{2-}(aq)] = s$ M. Hence:

$$K_{sp} = [Fe^{2+}(aq)][CO_3^{2-}(aq)] = (s)(s) = s^2 = 2.1 \times 10^{-11} \text{ or } s = 4.6 \times 10^{-6} \text{ M}$$

The formula mass of $FeCO_3$ is (55.85 (Fe) + 12.01 (C) + 3 × 16.00 (O)) g mol^{-1} = 115.86 g mol^{-1}. From above, 4.6×10^{-6} mol of $FeCO_3$ dissolves in 1.0 L. This corresponds to:

mass = number of moles × formula mass
= $(4.6 \times 10^{-6}$ mol) × (115.86 g mol^{-1}) = 5.3×10^{-4} g

This is the mass that dissolves in 1.0 L. The solubility is 5.3×10^{-4} g L^{-1}.

Answer: **5.3×10^{-4} g L^{-1}**

	Marks
• The concentration of iron in the ocean is one of the primary factors limiting the growth rates of some basic life forms. The pH of the oceans before the Industrial Revolution was around 8.22. What was the maximum concentration of Fe^{3+}(aq) in the ocean at this pH? The K_{sp} of $Fe(OH)_3$ is 1×10^{-39}.	**4**

As pH + pOH = 14.00, pOH = 14.00 – 8.22 = 5.78.

By definition, pOH = $-\log_{10}[OH^-(aq)]$ and so $[OH^-(aq)] = 10^{-5.78}$.

$Fe(OH)_3$ dissolves according to the equilibrium:

$$Fe(OH)_3 \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq) \quad \text{with } K_{sp} = [Fe^{3+}(aq)][OH^-(aq)]^3.$$

As $K_{sp} = 1 \times 10^{-39}$ and $[OH^-(aq)] = 10^{-5.78}$:
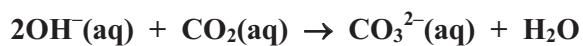
$$[Fe^{3+}(aq)] = K_{sp} / [OH^-(aq)]^3 = (1 \times 10^{-39}) / (10^{-5.78})^3 = 2 \times 10^{-22} \text{ M}$$

Answer: **2×10^{-22} M**

ANSWER CONTINUES ON THE NEXT PAGE

Industrialisation has led to an increase in atmospheric CO_2. What effect has this had on the amount of Fe^{3+}(aq) in sea water?

**CO_2 dissolves in water to give acidic solution that reacts with OH^- ions.**

$2OH^-$(aq) + CO_2(aq) → CO_3^{2-}(aq) + H_2O

From Le Chatelier's principle, the decrease in $[OH^-$(aq)] will result in an increase in $[Fe^{3+}$(aq)].

Equivalently, if $[OH^-$(aq)] is decreased, $[Fe^{3+}$(aq) must increase as K_{sp} is a constant.

- Solid sulfur can exist in both rhombic and monoclinic forms. A portion of the phase diagram for sulfur is reproduced schematically below.

Pressure (mm Hg)
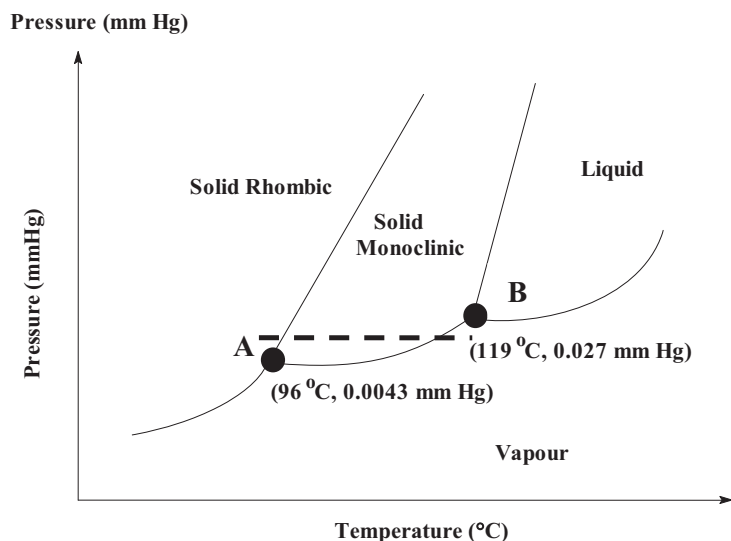
How many triple points are there in the phase diagram?   **2 (marked as dots)**

What phases are in equilibrium at each of the triple points?

(A) rhombic, monoclinic and vapour (at 96 °C and 0.0043 mmHg)
(B) monoclinic, liquid and vapour (at 119 °C and 0.027 mmHg)

What phase is stable at room temperature and 760 mmHg pressure?

solid rhombic

Can monoclinic sulfur exist in equilibrium with sulfur vapour at 1.0 atm pressure?

no

Which solid form of sulfur is more dense? Explain your reasoning.

Rhombic The equilibrium line between rhombic and monoclinic slopes to the right. Beginning in the monoclinic region close to this line and increasing the pressure, the line is crossed vertically into the rhombic region. As rhombic is more stable at higher pressure, it must be more dense than monoclinic.

Describe the phase changes that occur when sulfur at 0.01 mmHg is slowly warmed from 90 °C to 130 °C.

rhombic → monoclinic → vapour (see dotted line on phase diagram).

Marks
3

- An alloy is formed by combining elements A and B. The alloy has a face-centred cubic structure, with atoms of A at the corners and atoms of B in the faces. What is the formula of the alloy? Explain your reasoning.
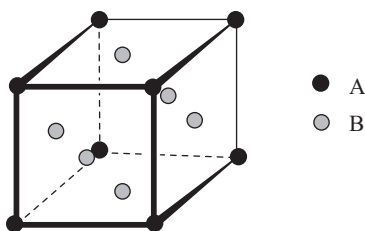
The atoms on the corners are shared between 8 cells: each contributes $^1/_8$.

The atoms on the faces are shared between 2 cells: each contributes $^1/_2$.

Thus, there are $8 \times {}^1/_8$ A atoms = 1 A atoms and $6 \times {}^1/_2$ B atoms = 3 B atoms.

Overall, A : B = 1 : 3 so the formula is AB_3.

● A
○ B

Answer: **AB_3**

3

- Derive expressions for the equilibrium constants for the complexation of Pb^{2+} (K_1) and of Ca^{2+} (K_2) by $EDTA^{4-}$.

$$\textbf{Pb}^{2+} + \textbf{EDTA}^{4-} \ \rightleftharpoons \ \textbf{[Pb(EDTA)]}^{2-} \quad K_1 = \frac{[\textbf{Pb(EDTA)}^{2-}]}{[\textbf{Pb}^{2+}][\textbf{EDTA}^{4-}]}$$

$$\textbf{Ca}^{2+} + \textbf{EDTA}^{4-} \ \rightleftharpoons \ \textbf{[Ca(EDTA)]}^{2-} \quad K_2 = \frac{[\textbf{Ca(EDTA)}^{2-}]}{[\textbf{Ca}^{2+}][\textbf{EDTA}^{4-}]}$$

Briefly explain why the chelating agent, EDTA, is administered as $[Ca(EDTA)]^{2-}$ to treat lead poisoning and determine which of K_1 or K_2 must be greater for the therapy to be effective.

**K_1 must be greater than K_2 for the therapy to be effective.**

$[Ca^{2+}]$ is much greater than $[Pb^{2+}]$ in the body, so need $K_1 > K_2$ to form the Pb complex. If EDTA is not administered as the Ca complex, it will strip Ca^{2+} from the body.

**Marks
8**

- Consider compound **F** shown below.
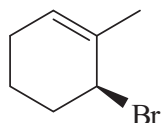
F

Assign the stereocentre in compound **F** as (*R*) or (*S*), explaining your reasoning.

(*S*) The four groups at the stereogenic centre are assigned priorities based on atomic numbers. Br has highest priority, H the lowest. The carbon labelled b, C(C,C,C) has higher priority than the carbon labelled c C(C,H,H) by examining the atoms attached to them. With d at the back, a→b→c is anticlockwise, so the configuration is (*S*).
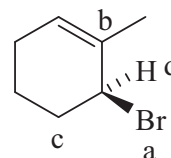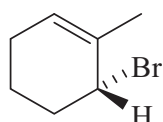

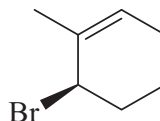Assign the double bond stereochemistry in compound **F**, explaining your reasoning.

(*Z*) Compare the priorities of the two groups at each end of the double bond: i.e. a1 with b1 and a2 with b2. The two low priority groups (b) are on the same side of the double bond, so the configuration is (*Z*).
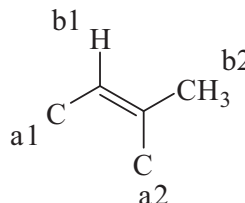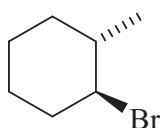
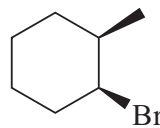

Draw the enantiomer of compound **F**.

or

When compound **F** is reacted with hydrogen gas in the presence of a palladium catalyst, two stereoisomeric products, **G** and **H**, are formed. Draw these products.


+

What word is used to describe the stereochemical relationship between **G** and **H**?

They are *diastereomers*. They differ in the arrangement of the bonds in space but are not mirror images.

Marks
5

- Bromide **A** undergoes a reaction with hydroxide ions (OH⁻) to produce alcohol **C**. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place in the conversion of **A** to **B** and from **B** to **C**.
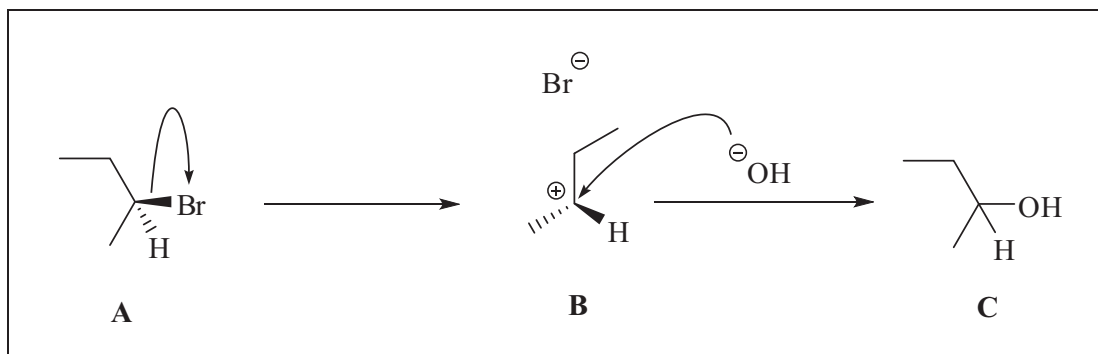

What is the name of the reaction taking place when **A** is converted to **C** via carbocation intermediate **B**?

S$_N$1 reaction (nucleophilic substitution, unimolecular)

What is the stereochemical outcome of this reaction? Give reasons for your answer.

The product is racemic because the intermediate carbocation (B) is planar.

Attack by OH⁻ is therefore equally likely from either top or bottom, leading to equimolar amounts of the two enantiomers.
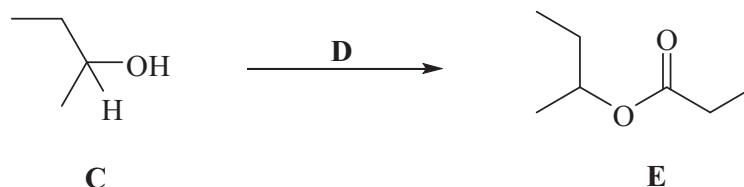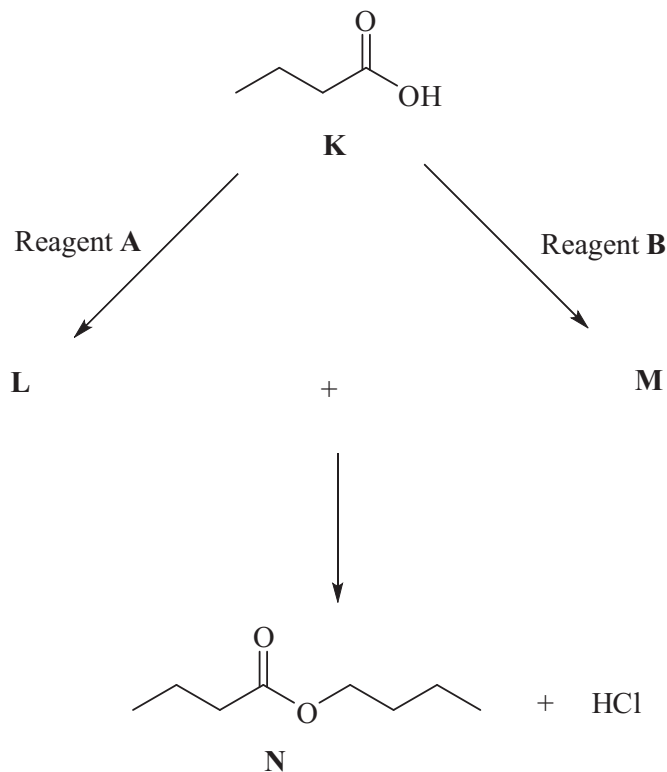

Alcohol **C** can be further reacted with reagent **D** to generate ester **E**. Provide a structure of a suitable reagent **D** for the synthesis of ester **E** from alcohol **C**.

The acid chloride, CH$_3$CH$_2$COCl , or the acid anhydride, (CH$_3$CH$_2$CO)$_2$O, would be used.

Marks
6

- Consider the following reaction sequence.

K

Reagent **A**   Reagent **B**

**L**   +   **M**

N   +   HCl

Compound **K** below can be converted into two different intermediates, **L** and **M**, which can react together to give compound **N** and the inorganic byproduct HCl. Give the reagents **A** and **B** and draw the structure of the intermediates **L** and **M**.

| A	B
SOCl₂	**1. LiAlH₄ / dry ether 2. H⁺ / H₂O**
L	M

Marks
3

- Give the constitutional formula(s) of the organic products formed in each of the following reactions

Marks
6
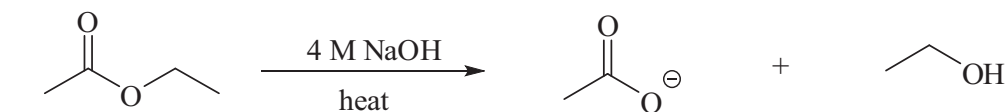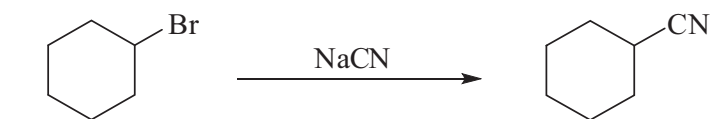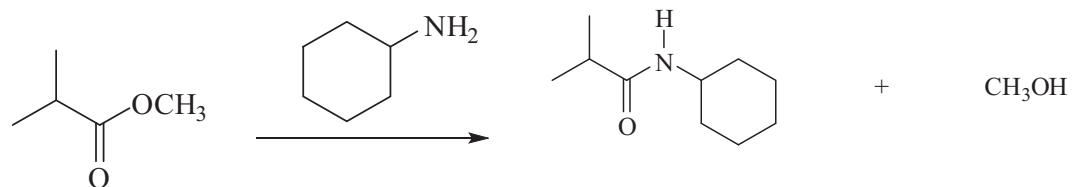
- Sketch the resonances you would expect to observe for protons H_B and H_C in the ^1H NMR spectrum of compound **X**. Ensure that the approximate chemical shifts, as well as peak splittings and signal integrations are incorporated in your answer. (The resonance for H_A is provided as a guide.)
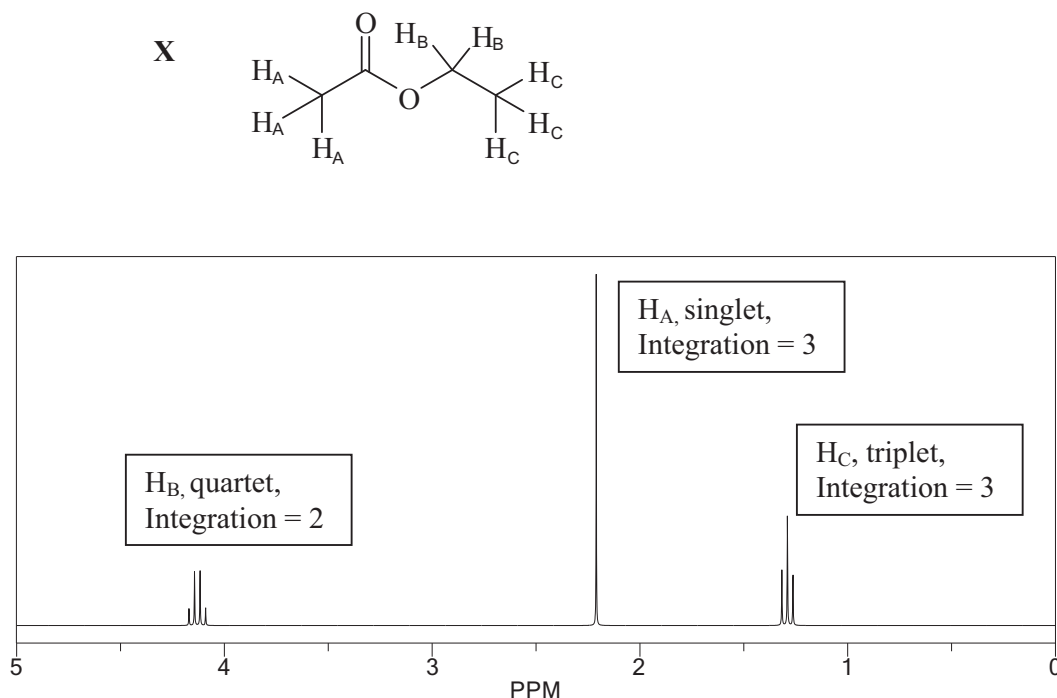
H_B have the highest shift since they are closest to the electronegative O atoms. There are two H_B atoms so the signal has an integral of 2. The H_B atoms are coupling to $3 \times H_C$ atoms giving rise to a $(n + 1) = (3 + 1) = 4$ line multiplet (a *quartet*).

H_C have the lowest shift since they are further from the electronegative O atoms. There are three H_B atoms so the signal has an integral of 3. The H_C atoms are coupling to $2 \times H_B$ atoms giving rise to a $(n + 1) = (2 + 1) = 3$ line multiplet (a *triplet*).

**Marks
5**

- Devise a synthesis of propylbenzene (**V**) using propanal (**T**) and bromobenzene (**U**) as starting materials. Provide any intermediate structures and reagents.
  (Hint: More than one step is required.)