

Topics in the November 2009 Exam Paper for CHEM1902

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- All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of the hydroxide, $\text{Fe}(\text{OH})_3$, which has a K_{sp} of only 2×10^{-39} .

Calculate the maximum possible concentration of $\text{Fe}^{3+}(\text{aq})$ in the pre-industrial era ocean which had a pH of about 8.2.

Marks
6

When pH = 8.2, pOH = 14.0 – 8.2 = 5.8. As pOH = $-\log_{10}[\text{OH}^-(\text{aq})]$:

$$[\text{OH}^-(\text{aq})] = 10^{-5.8} \text{ M}$$

$\text{Fe}(\text{OH})_3(\text{s})$ dissolves according to the chemical equation:



The solubility product is therefore given by:

$$K_{\text{sp}} = [\text{Fe}^{3+}(\text{aq})][\text{OH}^-(\text{aq})]^3$$

As $[\text{OH}^-(\text{aq})] = 10^{-5.8} \text{ M}$:

$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^3 = 2 \times 10^{-39} / (10^{-5.8})^3 \text{ M} = 5 \times 10^{-22} \text{ M}$$

$$[\text{Fe}^{3+}(\text{aq})] = 5 \times 10^{-22} \text{ M}$$

How many $\text{Fe}^{3+}(\text{aq})$ ions are present in a litre of seawater at this pH?

From above, $[\text{Fe}^{3+}(\text{aq})] = 5 \times 10^{-22} \text{ M} = 5 \times 10^{-22} \text{ mol L}^{-1}$. Hence, a litre of seawater contains $5 \times 10^{-22} \text{ mol}$.

The number of ions of Fe^{3+} is therefore:

$$\text{number of ions} = (5 \times 10^{-22} \text{ mol}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = 300$$

Answer: 300

The pH of the ocean is predicted to drop to 7.8 by the end of this century as the concentration of CO_2 in the atmosphere increases. What percentage change in the concentration of $\text{Fe}^{3+}(\text{aq})$ will result from this fall in pH?

When pH = 7.8, pOH = 14.0 – 7.8 = 6.2 and $[\text{OH}^-(\text{aq})] = 10^{-6.2} \text{ M}$. Hence:

$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^3 = 2 \times 10^{-39} / (10^{-6.2})^3 \text{ M} = 8 \times 10^{-21} \text{ M}$$

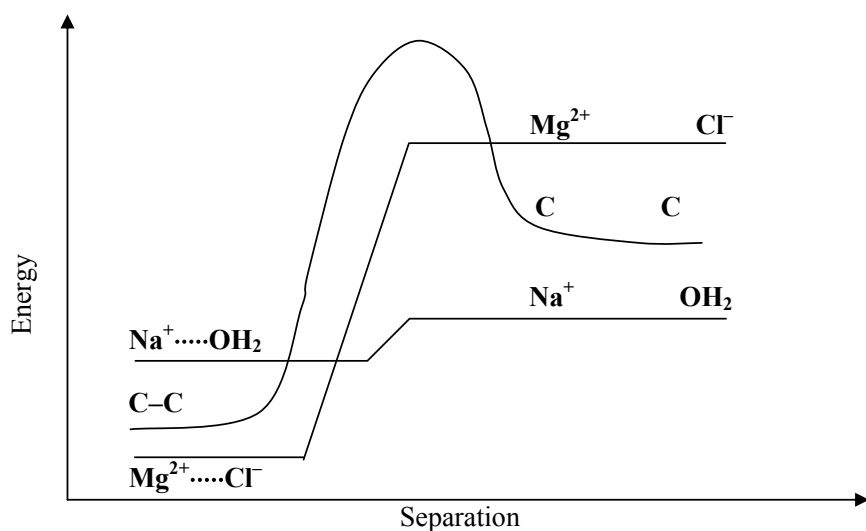
The percentage increase is therefore:

$$\text{percentage change} = \frac{(8 \times 10^{-21} - 5 \times 10^{-22})}{5 \times 10^{-22}} \times 100 \% = 1500 \%$$

Answer: 1500 %

- Shown below is the energy profile for the separation of Na^+ from H_2O . Draw energy profiles for the separation of Mg^{2+} from Cl^- and for the breaking of the C–C bond in ethane to the same scales (approximately).

Marks
6



There is an activation energy (barrier) for the breaking of a covalent bond. For an ionic bond and an ion-dipole interaction, the energy just increases with separation. Due to the charges, the ion-ion interaction is harder to break than the ion-dipole interaction.

Name the inter- or intra-molecular forces involved in each of these three interactions.

$\text{Na}^+ \text{ OH}_2$

ion - dipole

$\text{Mg}^{2+} \text{ Cl}^-$

ion – ion (ionic bond)

$\text{C} \text{ C}$

covalent bond

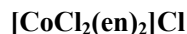
Explain why bonds such as C–C are generally considered to be stronger than interactions such as that between Mg^{2+} and Cl^- .

The covalent bond has a large energy barrier (activation energy) that must be overcome to break the bond. Ionic bonds do not have this barrier, but have a larger overall ΔH .

- When cobalt(II) chloride is reacted with ethane-1,2-diamine (en) and the product is oxidised in the air, a purple compound with the empirical formula $\text{CoCl}_3 \cdot 2\text{en}$ is obtained. When reacted with silver nitrate only one chloride ion is released. The compound can be resolved into its enantiomeric forms.

Marks
6

Give the structural formula of the compound.



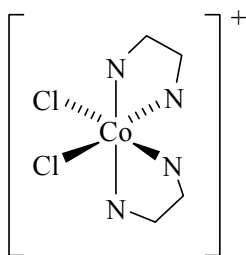
1 chloride ion must be a counter ion as only 1 is released when silver nitrate is added. As en is neutral, it must be coordinate to the metal ion.

Give the name of the compound.

***cis*-dichloridobis(ethane-1,2-diamine)cobalt(III) chloride**

Although the structural formula above gives rise to *cis* and *trans* isomers, only the *cis* form is optically active.

Draw the structure of the metal complex component of the compound.



What is the *d* electron configuration of the Co in this complex?

$[\text{CoCl}_2(\text{en})_2]\text{Cl} = \text{Co}^{3+} + 2\text{en} + 3\text{Cl}^-$. As Co is in group 9, it has 9 valence electrons. Co^{3+} has $(9 - 3) = 6$ electrons: $3d^6$

What types of isomers can be formed by a compound with this empirical formula?

Geometrical (*cis* and *trans*) isomers are possible.

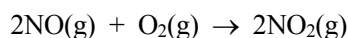
The *cis* isomer can form optical isomers.

Which of the possible isomers has formed? Explain the logic you have used in determining this.

As only the *cis* isomer can form enantiomers, it must have been formed.

The *trans* isomer is superimposable (i.e. identical) to its mirror image.

- Nitrogen monoxide, a noxious pollutant, reacts with oxygen to produce nitrogen dioxide, another toxic gas:



The following rate data were collected at 225 °C.

Experiment	[NO] ₀ (M)	[O ₂] ₀ (M)	Initial rate, -d[O ₂]/dt, (M s ⁻¹)
1	1.3×10^{-2}	1.1×10^{-2}	1.6×10^{-3}
2	1.3×10^{-2}	2.2×10^{-2}	3.2×10^{-3}
3	2.6×10^{-2}	1.1×10^{-2}	6.4×10^{-3}

Determine the rate law for the reaction.

Between experiments 1 and 2, [NO] is held constant and [O₂] doubles. This leads to a doubling of the rate: the reaction is 1st order with respect to O₂.

Between experiments 1 and 3, [O₂] is held constant and [NO] doubles. This leads to the rate increasing by a factor of 4: the rate is 2nd order with respect to NO.

The rate law is therefore:

$$-\text{d}[\text{O}_2]/\text{dt} = k[\text{NO}]^2[\text{O}_2]$$

Calculate the value of the rate constant at 225 °C.

In experiment 1, [NO] = 1.3×10^{-2} M, [O₂] = 1.1×10^{-2} M and rate = 1.6×10^{-3} M s⁻¹. Substituting these values into the rate law gives:

$$(1.6 \times 10^{-3} \text{ M s}^{-1}) = k \times (1.3 \times 10^{-2} \text{ M})^2 \times (1.1 \times 10^{-2} \text{ M})$$

Hence:

$$k = 860 \text{ M}^{-2} \text{ s}^{-1}$$

$$\text{Answer: } 860 \text{ M}^{-2} \text{ s}^{-1}$$

Calculate the rate of appearance of NO₂ when [NO] = [O₂] = 6.5×10^{-3} M.

Substituting the values into the rate law gives:

$$\begin{aligned} -\text{d}[\text{O}_2]/\text{dt} &= k[\text{NO}]^2[\text{O}_2] \\ &= (860 \text{ M}^{-2} \text{ s}^{-1}) \times (6.5 \times 10^{-3} \text{ M})^2 \times (6.5 \times 10^{-3} \text{ M}) = 2.35 \times 10^{-4} \text{ M s}^{-1} \end{aligned}$$

From the chemical equation, the rate of appearance of NO₂ is *twice* the rate of loss of O₂:

$$\text{d}[\text{NO}_2]/\text{dt} = 2 \times -\text{d}[\text{O}_2]/\text{dt} = (2 \times 2.35 \times 10^{-4} \text{ M s}^{-1}) = 4.7 \times 10^{-4} \text{ M s}^{-1}$$

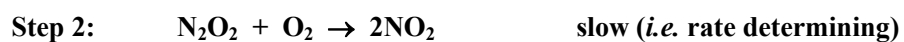
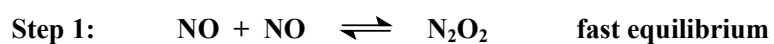
$$\text{Answer: } 4.7 \times 10^{-4} \text{ M s}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

Marks
7

Suggest a possible mechanism for the reaction based on the form of the rate law.
Explain your answer.

A possible mechanism is:



If the first step is at equilibrium with equilibrium constant K_1 :

$$K_1 = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \Rightarrow [\text{N}_2\text{O}_2] = K_1[\text{NO}]^2$$

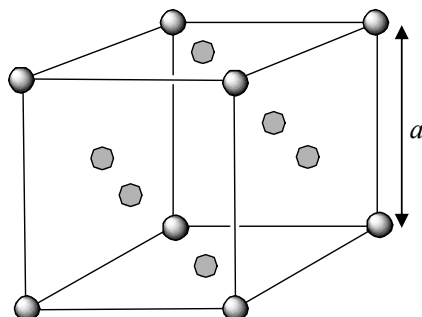
The rate of step 2 is therefore

$$\begin{aligned}\text{rate} &= k_2[\text{N}_2\text{O}_2][\text{O}_2] \\ &= k_2K_1[\text{NO}]^2[\text{O}_2]\end{aligned}$$

This is consistent with the experiment rate law with $k = k_1K$.

- The diagram below shows the structure of an alloy of copper and gold with a gold atom at each of the corners and a copper atom in the centre of each of the faces. The unit cell dimension (edge length, a) for this alloy is 0.36 nm.

Marks
5



● = Au

● = Cu

What is the chemical formula of the alloy?

There are 8 Au atoms on the corners. Each of these contribute 1/8 to the unit cell:

$$\text{number of Au atoms} = 8 \times 1/8 = 1$$

There are 6 Cu atoms on the face. Each of these contribute 1/2 to the unit cell:

$$\text{number of Cu atoms} = 6 \times 1/2 = 3$$

The ratio of Cu to Au atoms is therefore 3 : 1 and the formula is Cu_3Au .

Answer: **Cu_3Au**

Given that pure gold is 24 carat and gold alloyed with 25% by weight of another metal is termed 18 carat gold, what carat gold is this alloy?

The molar mass of Cu_3Au is:

$$\text{molar mass} = (3 \times 63.55 (\text{Cu}) + 1 \times 196.97 (\text{Au})) \text{ g mol}^{-1} = 387.62 \text{ g mol}^{-1}.$$

As 1 mol of Cu_3Au contains 1 mol of Au, the percentage by weight of gold in Cu_3Au is:

$$\text{percentage by weight} = \frac{197.67}{387.62} \times 100 \% = 50 \%$$

As a 100 % alloy is 24 carat and a 75% alloy is 18 carat, a 50 % alloy is 12 carat.

Answer: **12 carat**

What is the volume of the unit cell?

As the unit cell is cubic:

$$\text{volume} = (\text{side length})^3 = a^3 = (0.36 \times 10^{-9} \text{ m})^3 = 4.7 \times 10^{-29} \text{ m}^3$$

Answer: **$4.7 \times 10^{-29} \text{ m}^3$**

ANSWER CONTINUES ON THE NEXT PAGE

What is the density of the alloy?

From above, the unit cell contains 1 Au atom and 3 Cu atoms:

$$\text{mass of gold} = 196.97 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.271 \times 10^{-22} \text{ g}$$

$$\text{mass of copper} = 3 \times 63.55 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} = 3.166 \times 10^{-22} \text{ g}$$

$$\text{mass of unit cell} = (3.271 \times 10^{-22} + 3.166 \times 10^{-22}) \text{ g} = 6.437 \times 10^{-22} \text{ g}$$

The density is therefore:

$$\text{density} = \text{mass} / \text{volume}$$

$$= 6.437 \times 10^{-22} \text{ g} / 4.7 \times 10^{-29} \text{ m}^3 = 1.4 \times 10^7 \text{ g m}^{-3}$$

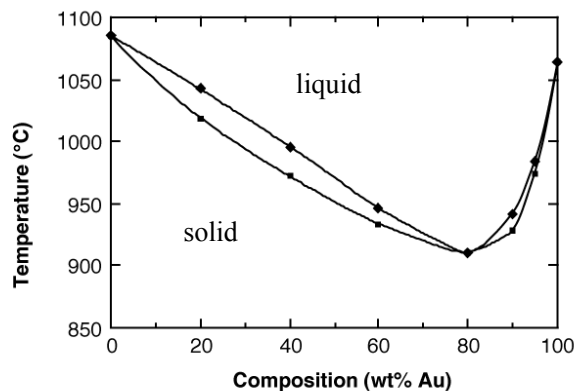
As 1 m = 100 cm, 1 m³ = (100)³ cm³ = 10⁵ cm³:

$$\text{density} = 14 \text{ g cm}^{-3}$$

Answer: 14 g cm⁻³

Shown below is the phase diagram for the Cu/Au system. Describe what would be seen as a sample of the alloy is heated from 900 to 1100 °C.

Marks
3

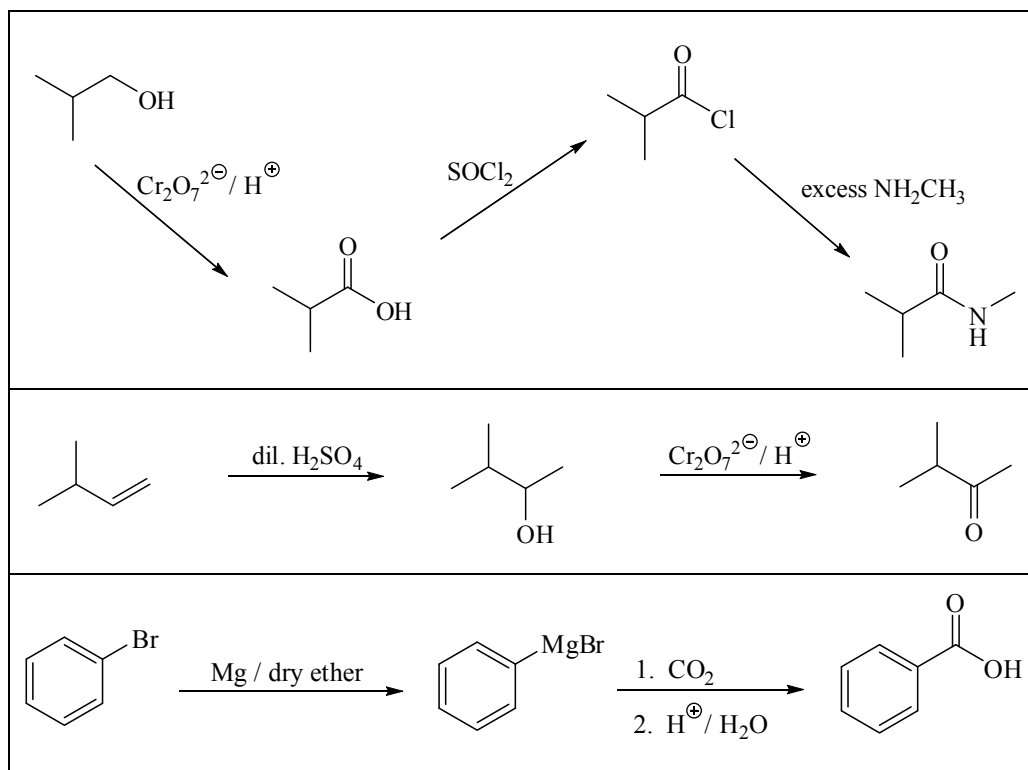


The solid would warm to 950 °C where melting would begin.

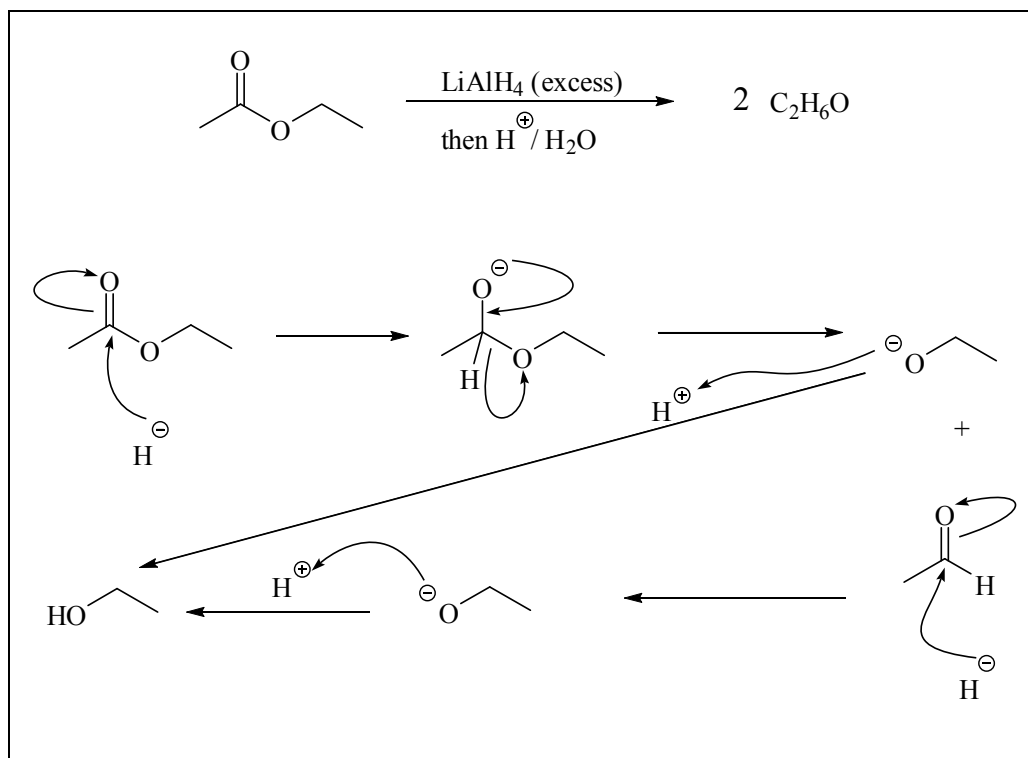
From 950 - 960 °C, the solid and liquid phases would co-exist. This should be compared to the behaviour of a pure substance where there is no increase in temperature whilst the solid melts.

Above 960 °C, only liquid is present.

- Suggest reagents to accomplish the following transformations. More than one step is required in all cases.

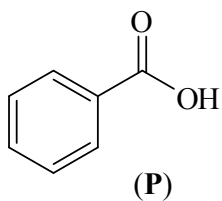
Marks
6

- Propose a structure for the product of the following reaction. Outline a mechanism for its formation. Show all curly arrows and any intermediates.

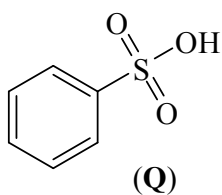
Marks
4

- For each of the following pairs of compounds, identify which is the stronger acid and give reasons for your choice.

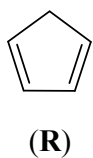
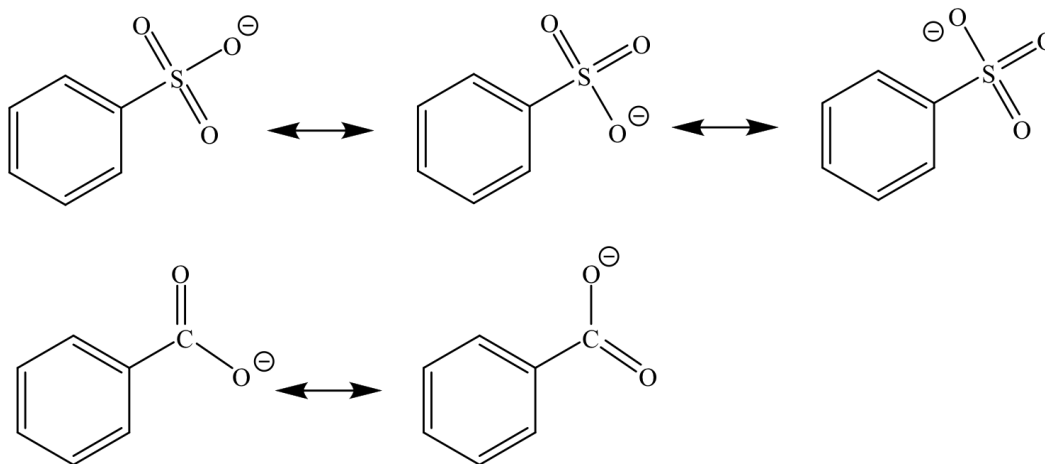
Marks
3



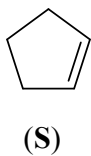
and



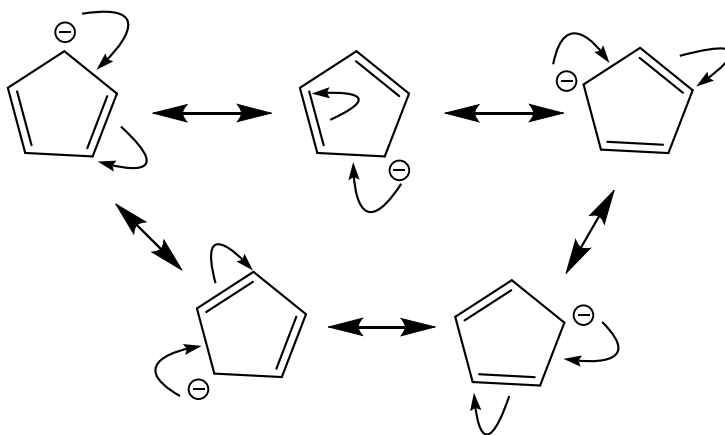
(Q) There is greater resonance stabilisation of the conjugate base (more canonical forms):



and



(R) There is greater resonance stabilisation of the conjugate base because it is aromatic.



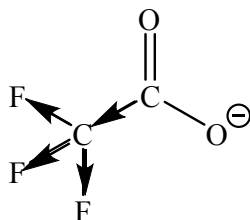
ANSWER CONTINUES ON THE NEXT PAGE

$\text{CF}_3\text{CO}_2\text{H}$ and $\text{CH}_3\text{CO}_2\text{H}$

(T)

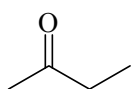
(U)

(T) There is greater resonance stabilisation of the conjugate base due to the inductive electron withdrawal of the very electronegative F atoms.

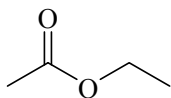


- The ^1H NMR spectra of these four compounds are shown below. Match each compound to its spectrum, and assign each spectrum as fully as you can.

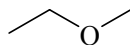
Marks
4



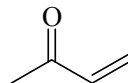
A



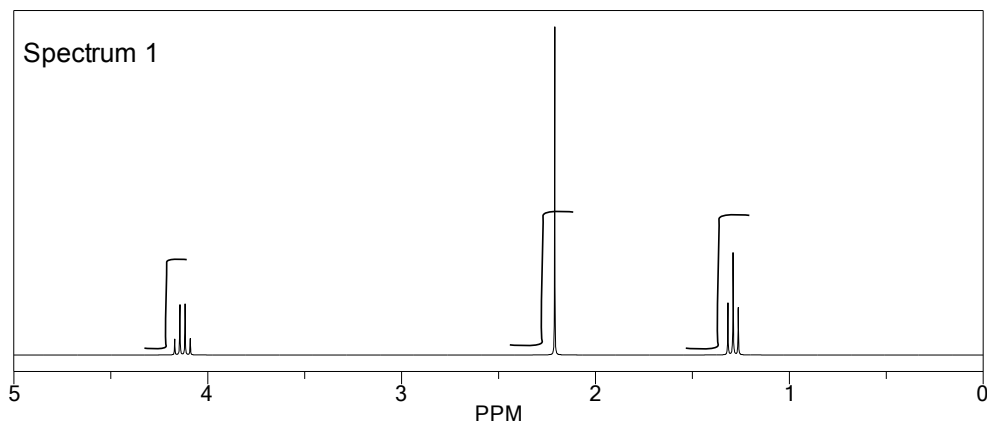
B



C

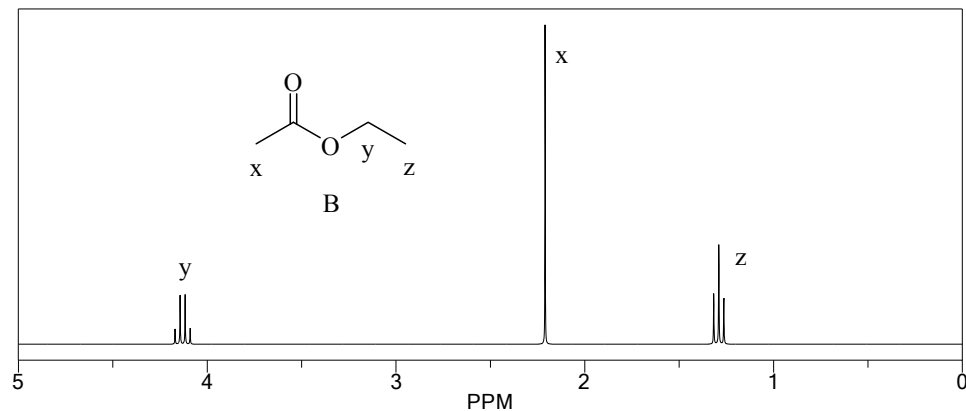


D



Spectrum of: A **B** C D (Circle the correct answer.)

Assignment:

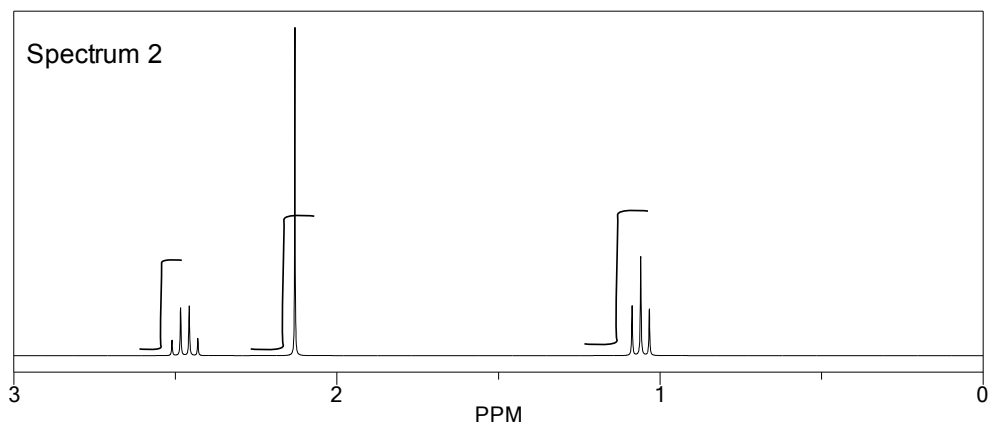


X is a CH_3 group (integral = 3) with no H atoms on neighbouring atoms: it is a singlet.

Y is a CH_2 group (integral = 2) with 3H on neighbouring atom; it is a quartet.

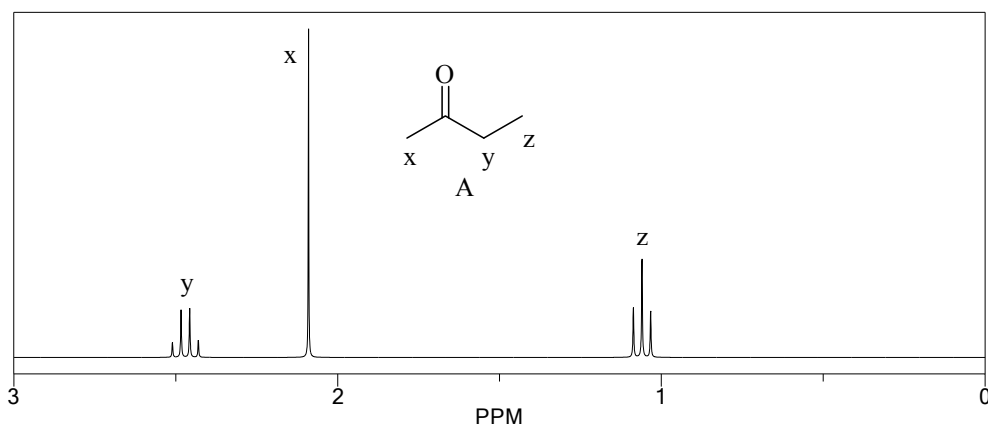
Z is a CH_3 group (integral = 3) with 2H on neighbouring atom: it is a triplet.

ANSWER CONTIUNES ON THE NEXT PAGE



Spectrum of: A B C D (Circle the correct answer.)

Assignment:

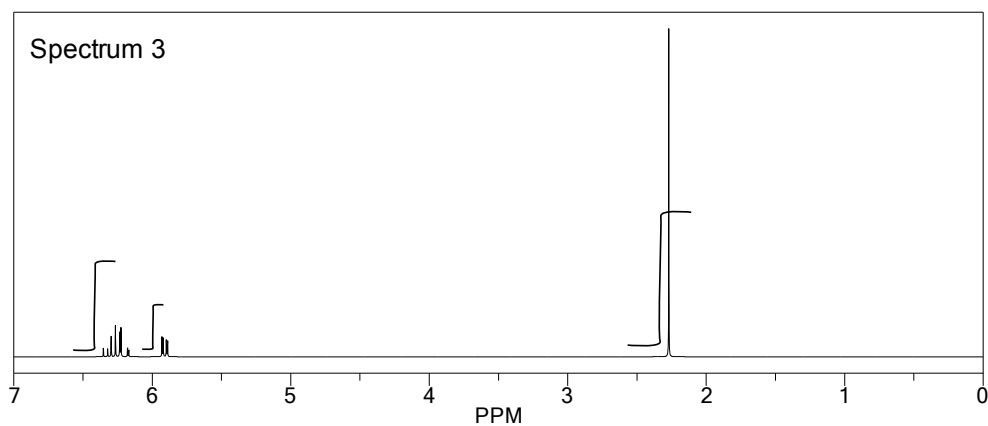


X is a CH₃ group (integral = 3) with no H atoms on neighbouring atoms: it is a singlet.

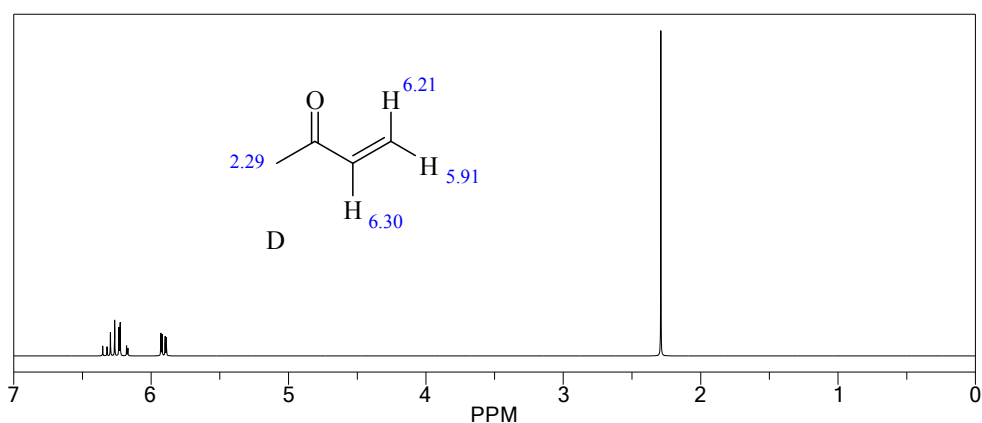
Y is a CH₂ group (integral = 2) with 3H on neighbouring atom; it is a quartet.

Z is a CH₃ group (integral = 3) with 2H on neighbouring atom: it is a triplet.

ANSWER CONTINUES ON THE NEXT PAGE

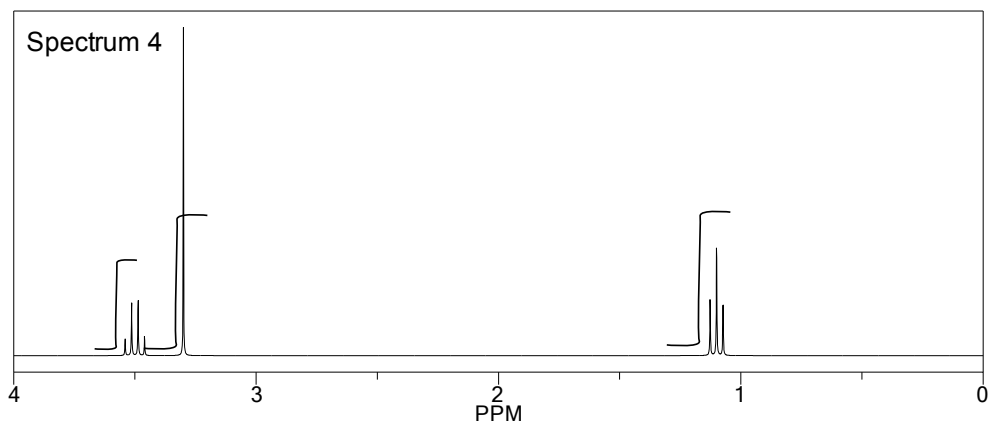
Marks
4Spectrum of: A B C D (Circle the correct answer.)

Assignment:



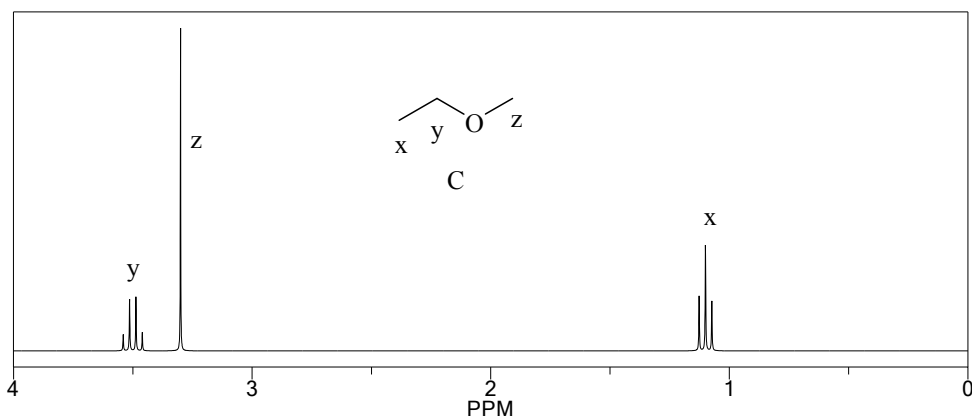
The correct assignments are as shown above, but level of knowledge in First Year only allows you to assign the singlet at 2.29 and the other 3 signals to the protons around the double bond.

ANSWER CONTINUES ON THE NEXT PAGE



Spectrum of: A B C D (Circle the correct answer.)

Assignment:

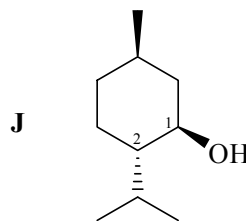


X is a CH₃ group (integral = 3) with 2H atoms on neighbouring atoms: it is a triplet.

Y is a CH₂ group (integral = 2) with 3H on neighbouring atom; it is a quartet.

Z is a CH₃ group (integral = 3) with no H atoms on neighbouring atoms: it is a singlet.

- The following questions pertain to the terpene natural product menthol (**J**), whose structure is shown. Carbons 1 and 2 are numbered to help you construct your answer.



**Marks
10**

Ignoring the stereochemistry, what is the systematic name for menthol?

2-isopropyl-5-methylcyclohexanol

2-(1-methylethyl)-5-methylcyclohexanol is also acceptable.

Assign the absolute configuration at C1 and at C2. Explain your reasoning.

C1 is (R)

Priorities: OH > C2 C(C,C,H) > C6 C(C,H,H) > H

With H at back, the order of –OH → –C2 → –C6 goes clockwise

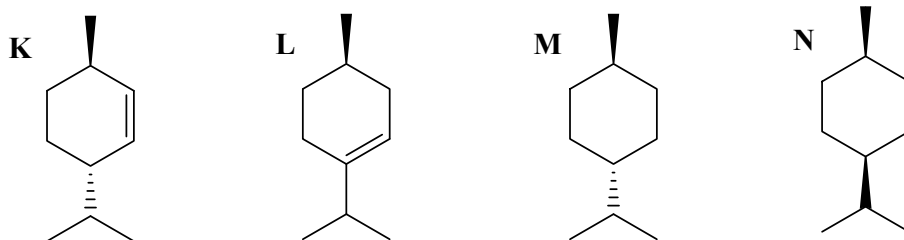
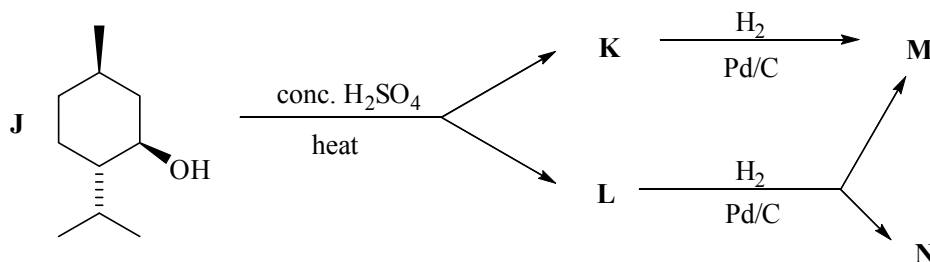
C2 is (S)

Priorities: C1 C(O,C,H) > isopropyl C(C,C,H) > C3 C(C,H,H) > H

Remember the H is pointing in front of the paper.

With H at back, the order of –C1 → –CH(CH₃)₂ → –C3 goes anticlockwise

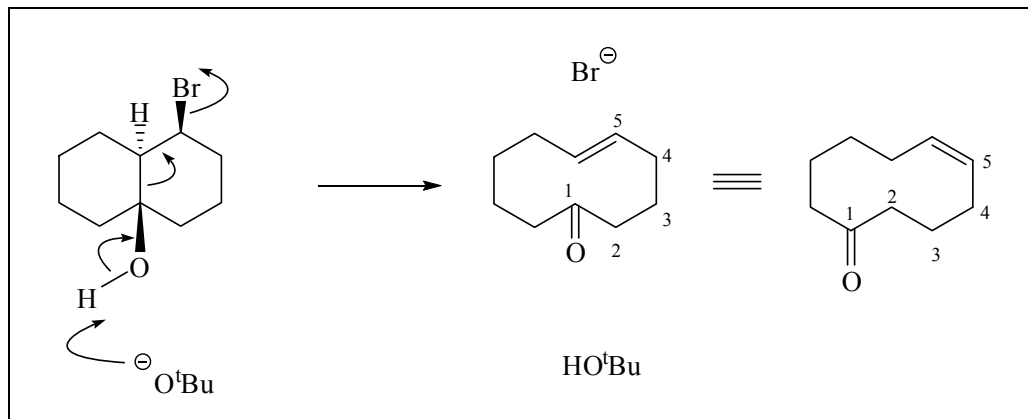
When menthol (**J**) is heated with concentrated sulfuric acid, two isomeric products **K** and **L** are formed. When **K** and **L** are treated with excess H₂ in the presence of a Pd/C catalyst, two products **M** and **N** are observed: **K** gives only **M**, while **L** gives a mixture of **M** and **N**. Propose structures for **K**, **L**, **M** and **N**.



ANSWER CONTINUES ON THE NEXT PAGE

What is the isomeric relationship between K and L ?	constitutional isomers
What is the isomeric relationship between M and N ?	diastereoisomers
Which (if any) of the compounds J , K , L , M and N are optically active?	J, K and L

- Add curly arrows to complete the mechanism of the unusual E2 reaction shown below, the Grob Fragmentation. (Note that KO^tBu is potassium *tert*-butoxide, a strong base.)

**Marks
3**

Explain briefly why the relative stereochemistry of the OH and Br groups in the starting material is important in this reaction.

The groups must have an antiperiplanar alignment in order that the orbitals overlap correctly to form the new bonds.