

Topics in the November 2009 Exam Paper for CHEM1002

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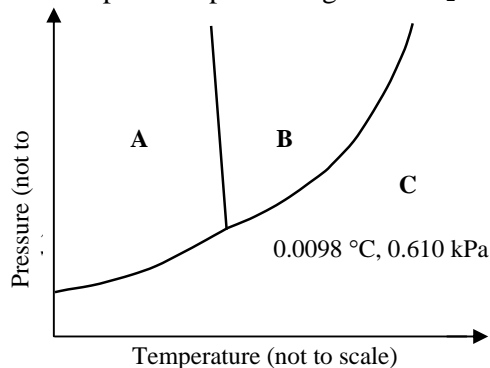
2009-N-11:

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- Consider the pressure/temperature phase diagram of H₂O shown below.



Which phase exists in the fields labelled **A**, **B** and **C**?

A: solid

B: liquid

C: gas

What are the temperature and pressure for the normal boiling point of water?

100 °C and 1 atm

Use the phase diagram to explain why it takes longer to hard boil eggs on the top of a 6000 m high mountain rather than at sea level.

The air pressure is lower at 6000 m than at sea level.

The boundary line between regions B and C shows that lowering the pressure lowers the boiling point. When the water is boiling, it will be at a lower temperature at 6000 m than at sea level.

If the temperature is lower, a longer period of time is required to effect the same level of cooking.

The unusual property of water, with the solid being less dense than the liquid, can be deduced from the phase diagram. How?

The equilibrium line between the solid and the liquid (represented by the line between regions A and B) slopes to the left.

If you begin in the solid region close to this line and you increase the pressure, you will cross the line vertically and go into the liquid region.

The liquid is *more* stable at *higher* pressure so it must be more dense than the solid.

Marks

6

- The periodic table lists elements in a systematic fashion. Briefly explain why the atomic radii decrease in period 3 (Na → Cl) from left to right.

Marks
3

Across a period, more electrons get added to the same electron shell and the number of protons in the nucleus increases. This leads to an increase in the effective nuclear charge.

The electrons therefore get attracted more strongly to the nucleus and the radius decreases.

What consequence does the shrinking atomic size have for the nature and reactivity of these elements?

As the electrons get held more strongly, there is a gradual change from metallic to non-metallic behaviour.

The smaller atoms attract additional electrons more strongly and have a higher electronegativity.

The increase in effective nuclear charge leads to an increase in the ionization energy across the period. This leads to decreasing reactivity across the first few groups. As the period is crossed, the elements become increasingly electronegative with increasing electron affinities. This leads to an increased reactivity from the middle of the period toward the end.

The full shell and high effective nuclear charge at the end of the period leads to very low reactivity for the last group.

- Conjugate acid/base pairs exist in aqueous solutions of weak acids. What is the difference between a weak acid and its conjugate base?

4

An acid and its conjugate base differ by a proton (H^+). The conjugate base of an acid has *one less proton*.

How are the strength of a weak acid and its conjugate base related?

The weaker the acid, the stronger the conjugate base: $K_a \times K_b = 10^{-14.00}$

From the following list select 2 conjugate acid/base pairs. Identify acid and base in both pairs.



acid	base
H_3PO_4	$H_2PO_4^-$
H_2CO_3	HCO_3^-
$H_2PO_4^-$	HPO_4^{2-}

- You have completed a number of acid/base titrations during your laboratory work. What is the difference between the 'end point' and the 'equivalence point' in an acid/base titration?

Marks
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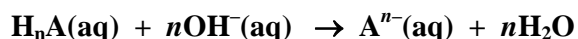
The endpoint is where the indicator changes colour and the reaction is observed to be completed. The equivalence point is where equal amounts of acid and base have been added. Ideally, the endpoint and equivalence point should be as close to one another as possible.

How do you determine the concentration of a weak acid through titration with a strong base? Include all necessary steps in your explanation.

Place a known volume (eg 25.00 mL) of the weak acid solution in a conical flask and add 2 drops of a suitable indicator (such as phenolphthalein).

Titrate with a known concentration of the strong base from a burette until the end point (the first *permanent* pink colour) is reached. Record the volume used.

The equation of the reaction must be known



This can then be used to calculate the moles of OH^- used.

Hence calculate the moles of weak acid present in 25.00 mL.

Hence calculate the moles of weak acid present in 1000.00 mL (i.e. its concentration).

How do you determine the pK_a of a weak acid through titration with a strong base? Include all necessary steps in your explanation.

The titration described above is used and the titration of the weak acid is continued past its equivalence point with a strong base, recording the pH as you go.

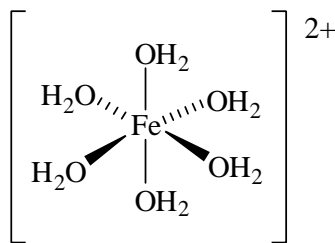
Construct a graph of mL base added vs pH. This is a titration curve.

Determine the volume of base required to reach equivalence point (where slope of line is vertical).

Divide this value by 2 to give the half equivalence point (where $[\text{HA}] = [\text{A}^-]$).

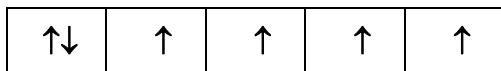
Read the value of the pH at the half equivalence point from the titration curve. From Henderson-Hasselbalch equation, this is the point where $\text{pH} = \text{pK}_a$.

- Dissolution of iron(II) chloride in water leads to formation of $\text{Fe}^{2+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ ions. Draw a picture of the complex ion present, clearly showing the stereochemistry and which atoms are bonded to the $\text{Fe}(\text{II})$ ion.



This complex is paramagnetic. Using the box notation to represent atomic orbitals, account for this property.

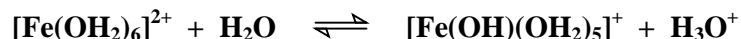
Fe is in group 8: it has 8 valence electrons. Fe^{2+} has lost 2 so has $(8 - 6) = 2$ electrons: d^6 . These are arranged in the 5 available d orbitals to maximize the number of unpaired electrons and so minimize the electron – electron repulsion, as shown below.



Paramagnetism occurs whenever there are unpaired electrons.

Solutions containing the $\text{Fe}^{2+}(\text{aq})$ ion are acidic. Account for this property and write the chemical equation for the reaction that leads to this acidity.

Fe^{2+} has a reasonably high charge density and this polarises the $\text{Fe}-\text{OH}_2$ bonds. This in turn weakens the $\text{O}-\text{H}$ bonds and leads to H^+ being released.



Marks
2

- Assuming aspirin has a half life of around 3 hours in the body, how much of an 80 mg dose will still be in the body after 1 day?

The amount of aspirin halves every 3 hours.

If the initial amount is 80 mg, there will be 40 mg after 3 hours. It continues to halve every 3 hours.

time / hours	amount / mg
0	80
3	40
6	20
9	10
12	5
15	2.5
18	1.25*
21	0.625*
24	0.3125*

The initial dose of 80 mg was only measured to 1 significant figure and so the answer is also only known to this level of accuracy. There is 0.3 mg left after 1 day.

*** To avoid rounding errors, these numbers are given in full and the rounding to 1 significant figure is left until the end.**

Answer: **0.3 mg**

- The pH of the ocean before the industrial revolution was around 8.22. Show that this pH corresponds to a concentration of $[\text{OH}^-(\text{aq})] = 1.7 \times 10^{-6} \text{ M}$.

Marks
6

By definition, $\text{pH} = -\log_{10}[\text{H}^+(\text{aq})]$. Hence, a pH of 8.22 corresponds to:

$$[\text{H}^+] = 10^{-\text{pH}} \text{ M} = 10^{-8.22} \text{ M}$$

$[\text{H}^+(\text{aq})]$ and $[\text{OH}^-(\text{aq})]$ are linked through K_w . Assuming a temperature of 298 K,

$$K_w = [\text{H}^+(\text{aq})][\text{OH}^-(\text{aq})] = 1.00 \times 10^{-14}$$

Hence:

$$[\text{OH}^-] = K_w / [\text{H}^+(\text{aq})] = 1.00 \times 10^{-14} / 10^{-8.22} \text{ M} = 1.7 \times 10^{-6} \text{ M}$$

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 1×10^{-39} . What was the maximum concentration of $\text{Fe}^{3+}(\text{aq})$ at a pH of 8.22?

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



The solubility product is therefore given by:

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

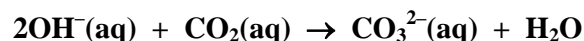
As $[\text{OH}^-(\text{aq})] = 1.7 \times 10^{-6} \text{ M}$:

$$[\text{Fe}^{3+}(\text{aq})] = K_{\text{sp}} / [\text{OH}^-(\text{aq})]^3 = 1 \times 10^{-39} / (1.7 \times 10^{-6})^3 \text{ M} = 2 \times 10^{-22} \text{ M}$$

Answer: $2 \times 10^{-22} \text{ M}$

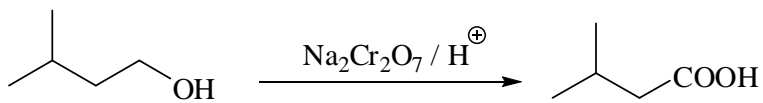
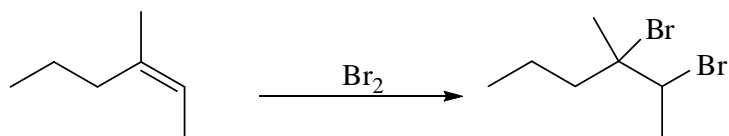
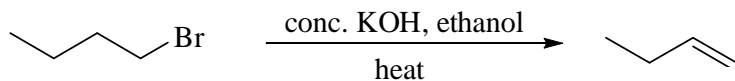
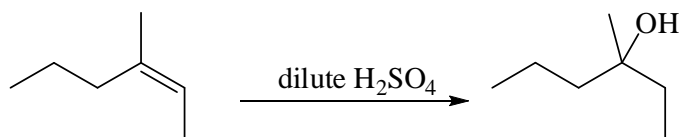
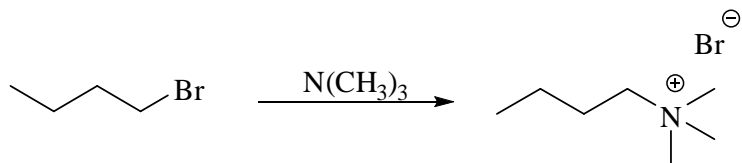
Industrialisation has led to an increase in atmospheric CO_2 . What effect has this had on the amount of $\text{Fe}^{3+}(\text{aq})$ in sea water?

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



Increased amounts of CO_2 is thus likely to decrease the amount of OH^- in the sea water. From Le Chatelier's principle, the decrease in $[\text{OH}^-]$ will result in the equilibrium for the dissolution of $\text{Fe}(\text{OH})_3$ above shifting to the right. This will lead to an increase in $[\text{Fe}^{3+}(\text{aq})]$.

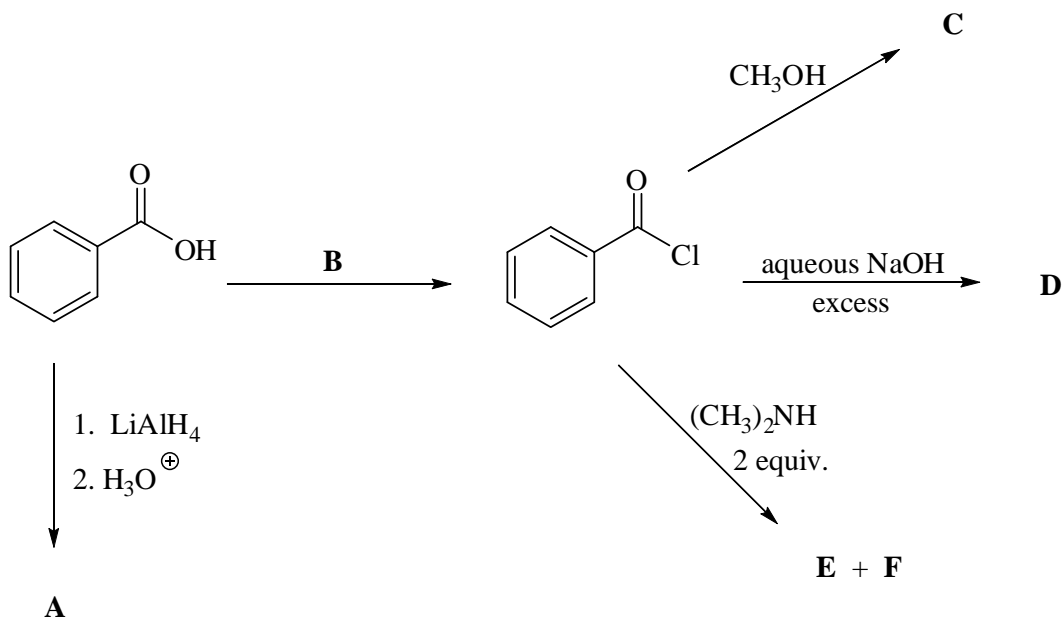
- Give the name of the starting material where indicated and the constitutional formula of the major organic product formed in each of the following reactions.

Marks
8**Name: 3-methyl-1-butanol****Name: (Z)-3-methyl-2-hexene****Name: 1-bromobutane**

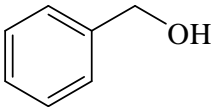
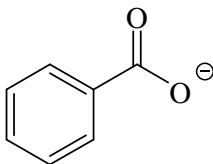
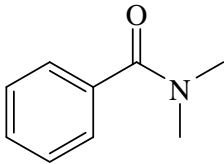
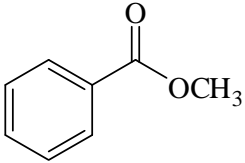
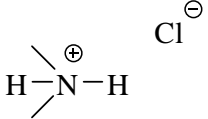
- Consider the following reaction sequence.

Marks

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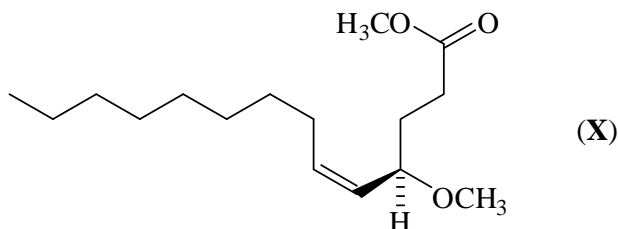


Give the reagent **B** and draw the constitutional formulas of the major organic products, **A**, **C**, **D**, **E** and **F**, formed in these reactions.

A 	D 
B SOCl_2	E 
C 	F 

- Compound (**X**) is a derivative of a naturally occurring Japanese beetle pheromone.

Marks
7



What is the molecular formula of (**X**)?

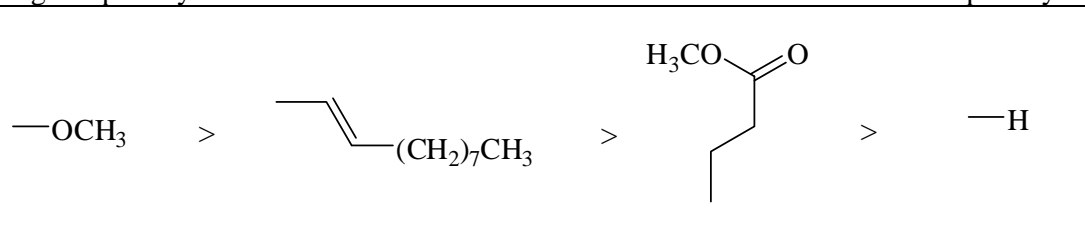
C₁₆H₃₀O₃

What is the stereochemistry of the C–C double bond in (**X**)? (**Z**)

List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rule.

highest priority

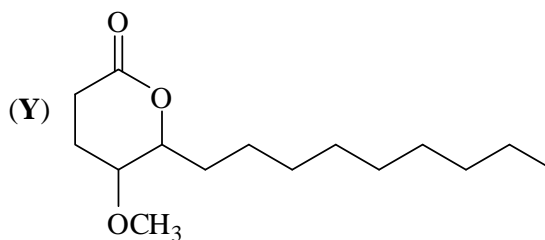
lowest priority



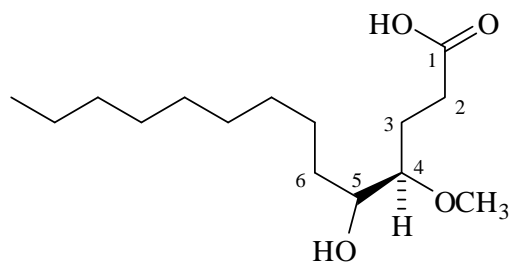
What is the absolute stereochemistry of (**X**)? Write (*R*) or (*S*).

(*R*)

On heating with 4 M H₂SO₄, one of the products obtained is compound (**Y**), whose structure is shown on the right. Explain the formation of this product.

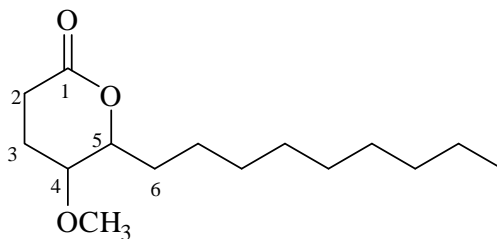


The 4 M H₂SO₄ catalyses 2 reactions; (i) hydrolysis of the ester to a carboxylic acid and (ii) addition of water across the C=C double bond to give the following intermediate:



ANSWER CONTINUES ON THE NEXT PAGE

This intermediate can undergo an intramolecular esterification (the OH on carbon 5 reacts with the carboxylic acid group at carbon 1) to give the cyclic ester (Y).

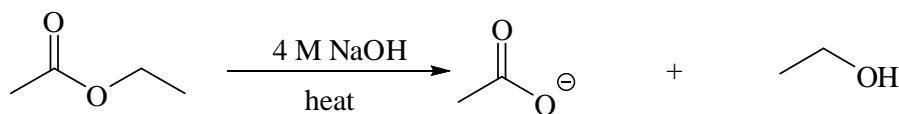
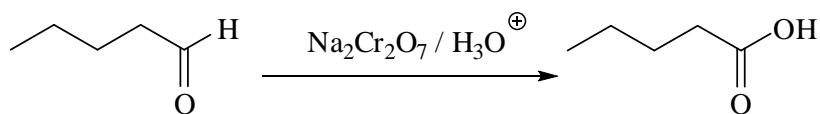
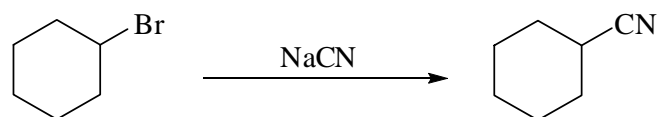
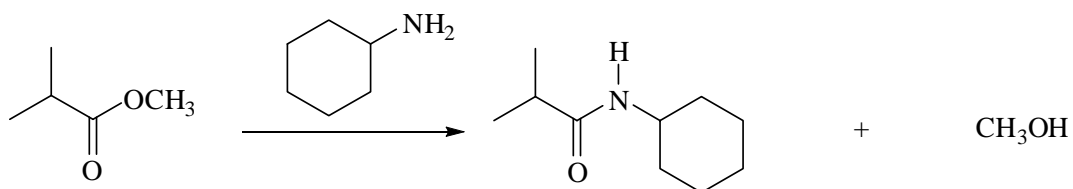


How many different stereoisomers are possible for compound (Y)?

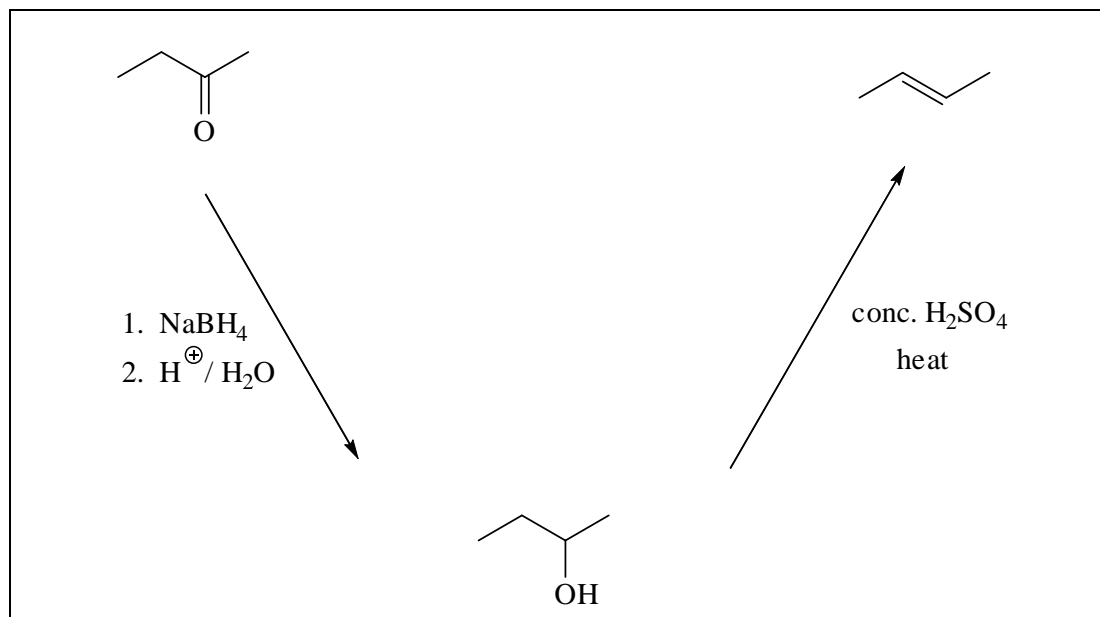
4*

*There are stereogenic centres at C4 and C5.

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



- Show clearly the reagents you would use to carry out the following chemical conversion. Two steps are required. Give the structure of the intermediate compound.

Marks
8

How can IR spectroscopy distinguish between the starting material, the intermediate and the product?

The starting material absorbs strongly in the 1650-1800 cm⁻¹ region due to the presence of the carbonyl (C=O) group.

The intermediate absorbs strongly in the 3000-3300 cm⁻¹ region due to the presence of the alcohol (O-H) group .

The product does not absorb strongly in either of these regions.

How can ¹³C NMR spectroscopy distinguish between the starting material, the intermediate and the product?

The product is symmetrical and has only 2 resonances.

The starting material and the intermediate both have 4 resonances, but the chemical shifts will differ: the carbonyl C in the starting material is at higher chemical shift (180-200 ppm) than the C-OH carbon (~50 ppm).