SYDNEY BOYS HIGH SCHOOL

2022 **POST-TRIAL EXAMINATION**

Chemistry

General Instructions

- Reading time – 5 minutes
- Working time – 1 hour
- Write using black pen
- Draw diagrams in pencil
- Calculators approved by NESA may be used
- A formula sheet, data sheet and Periodic Table are NOT provided at the back of this paper – print your own

Total Marks: 38

Section I – 4 marks

- Attempt Questions 1-4
- Allow about 10 minutes for this section

Section II – 34 marks

- Attempt questions 6-12
- Allow about 50 minutes for this section

Examiner: Donny

Section I

5 marks

Attempt Questions 1–5
Allow about 10 minutes for this section

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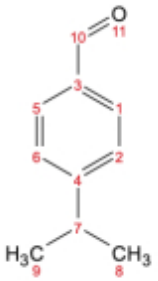
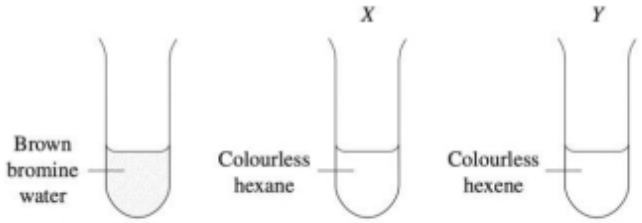
1 How many ^{13}C NMR peaks would you expect from the following compound?



A. 7
B. 8
C. 9
D. 10

2 Three test tubes were set up as shown.



All three liquids were then transferred to ONE test tube. How many phases (distinct layers) would be present in this new test tube?

A. 1
B. 2
C. 3
D. 4

3. When purifying an ester he made in class, a student used NaOH instead of Na_2CO_3 to react off the excess acid. How would the yield of the ester be affected?

A. Decreases
B. Increases
C. No effect
D. Can't tell

4. It is known that amine groups are able to protonate and increase the pH of a solution. What would the pH of an amide approximately be?

A. 7
B. 8
C. 9
D. Depends on what the amide is.

Section II

34 marks

Attempt Questions 5–11
Allow about 50 minutes for this section

Question 5 (5 marks)

(a) Calculate the concentration of hydroxide ions present in pure water at 25°C. **1**

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(b) Calculate the water solubility of $Fe(OH)_3$ at 25°C, given that $K_{sp} = 2.0 \times 10^{-39}$ **4**
[Hint: consider part (a)].

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Question 6 (5 marks)

Sodium metal was added to dehydrated **A** and effervescence was observed due to the evolution of **B**. When **A** is reacted with acidified potassium dichromate solution, a colour change from orange to green was observed. However, no observable changes were seen when Lucas' reagent was added to **A**. The mass spectrum of **A** has a parent ion peak at 60 (m/z). **5**

B was then reacted with **C** to form **D**. When **C** is reacted with water, only 1 isomeric product forms (i.e. no minor product). **C** gives two peaks in a ^{13}C NMR. **D** is then sent through a mass spectrometer and a peak at 43 (m/z) was seen, corresponding to **E**.

Draw the structural formulae for compounds **A** to **E**

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Question 7 (6 marks)

Consider a solution that contains both 0.10 M Na_2SO_4 and 0.10 M NaI. A solution containing Pb^{2+} ions is added dropwise at a constant rate to this solution. You may assume that the volume change due to the addition of this Pb^{2+} solution is negligible.

(a) At what concentration of Pb^{2+} will the first sign of precipitation be observed? **2**

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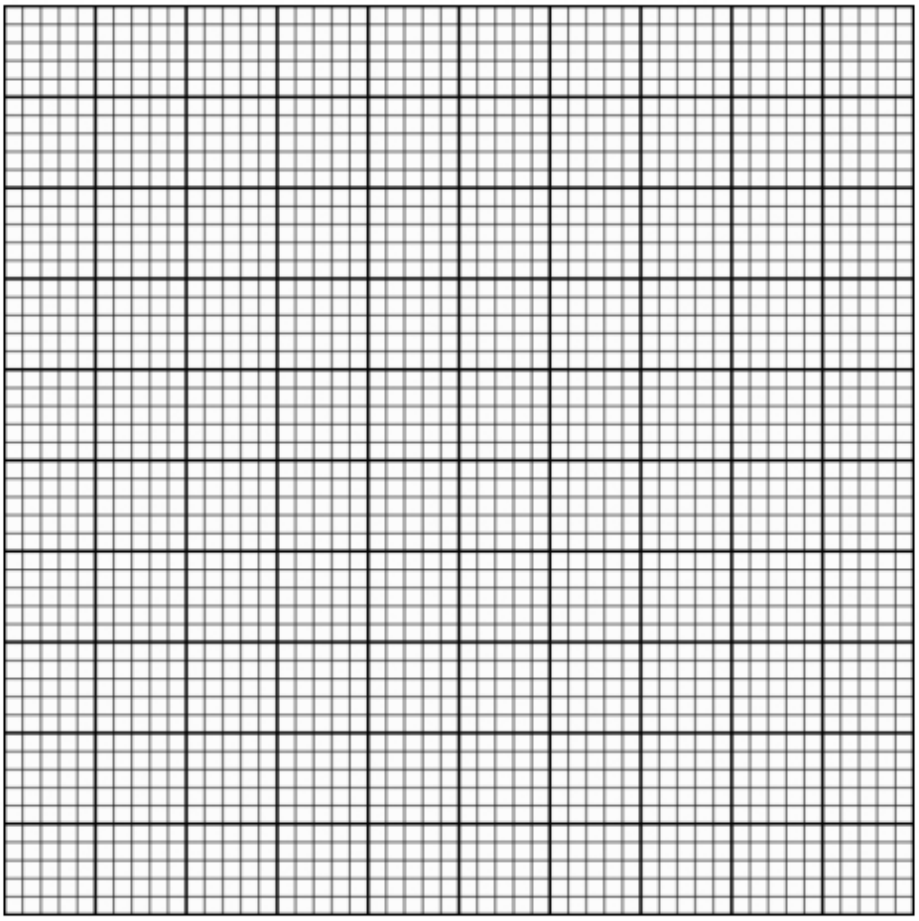
(b) On the graph below, sketch how the Pb^{2+} concentration will change over time. Quantitatively label the concentration thresholds where the salt being precipitated changes. You do NOT need to title the graph; however, axes labels are required. **4**



Question 8 (3 marks)

A student titrates 30.00 mL of 0.1000 M HCl with 0.1500 M NH_3, where $pK_b(NH_3) = 4.76$. **3**

Calculate the pH after 15.00 mL of NH_3 is added

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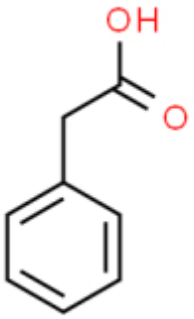
Question 9 (3 marks)

The figure below shows the structure of phenylacetic acid – a crucial chemical for the synthesis of methamphetamine (commonly known as crystal meth). **3**



Using the chemicals listed below (some may not be required), propose a possible reaction pathway to synthesise phenylacetic acid.

- sodium hydroxide
- ethene
- propyne
- benzene
- styrene
- water
- Lucas' reagent
- acidified potassium permanganate
- concentrated sulfuric acid
- dilute sulfuric acid

You may use skeletal formulae.

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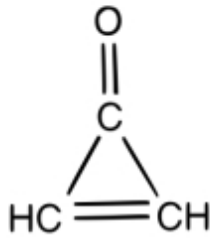
Question 10 (4 marks)

The double bond equivalence (DBE) of a compound is equal to the amount of double bonds plus the number of rings it contains. For example, the compound depicted below has a double bond equivalence of 3.



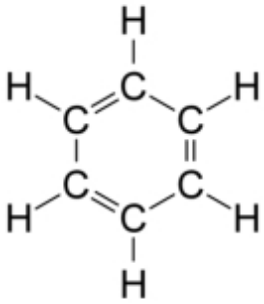
The double bond equivalence of any compound can be calculated using:

$$\mathrm{DBE} = \mathrm{C} - \frac{\mathrm{H}}{2} - \frac{\mathrm{X}}{2} + \frac{\mathrm{N}}{2} + 1$$

where,

- C = number of carbon atoms
- H = number of hydrogen atoms
- X = number of halogen atoms
- N = number of nitrogen atoms

(a) State the double bond equivalence of benzene given its structure below. **1**



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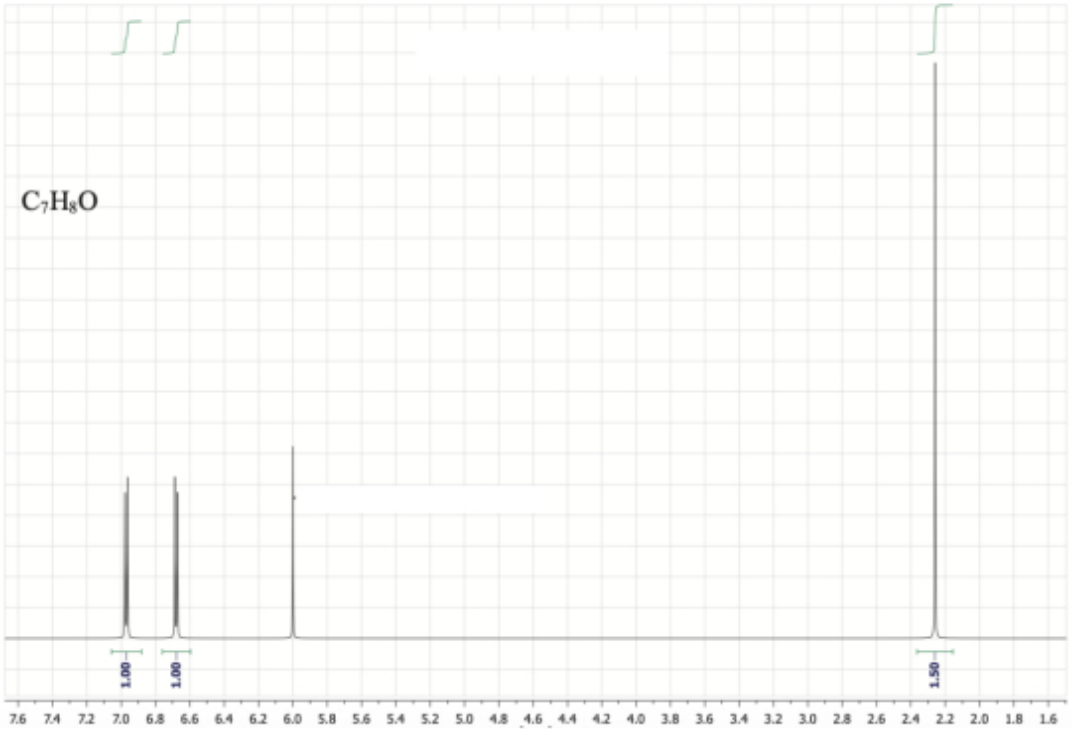
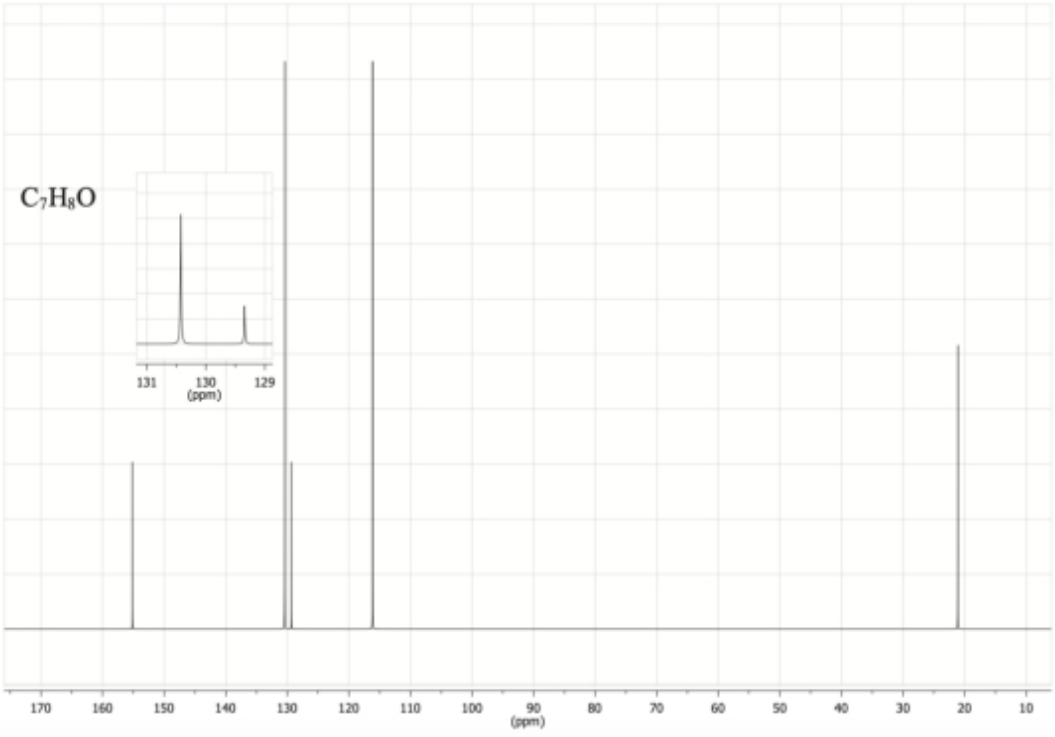
Question 16 continues on the next page

(b) A compound **X** with molecular formula C_7H_8O has the following ^1H NMR and ^{13}C NMR spectra: **3**

^1H NMR



^{13}C NMR



(b) Draw the structure of compound X. You may NOT use a data sheet with ^{1}H NMR chemical shifts.

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Question 11 (9 marks)

Consider the following reversible reaction with $K_c = 8.30 \times 10^{-4}$

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$$

(a) Calculate the equilibrium concentrations for each species if initially there was only 0.10 M of $COCl_{2(g)}$ in the system. **3**

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(b) Would the equilibrium concentrations be the same if instead the system began with only 0.10 M $CO_{(g)}$ and 0.10 M $Cl_{2(g)}$? **1**

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Question 17 continues on the next page

(c) Calculate the equilibrium concentration of $COCl_{2(g)}$ in a system beginning with 0.15 M $CO_{(g)}$ and 0.25 M $Cl_{2(g)}$. You may NOT use the quadratic formula. [Hint: use the idea from part (b)] **5**

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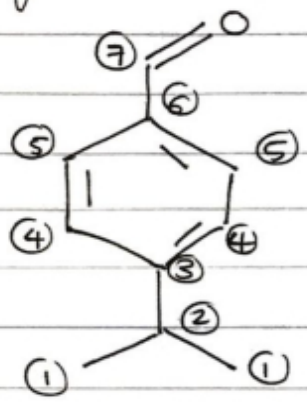
Question 1

Due to symmetry of molecule, some carbon environments are equivalent:



∴ Key is (A)

Question 2 Trick question: in organic reactions, you can really only have an organic or aqueous layer.

Hexane doesn't react with Br_2 in absence of UV light, so it forms an organic phase

Br_2 reacts with hexene to form a dibromo substituted hydrocarbon which forms aqueous phase with other species in bromine water.

∴ Key is (B)

Question 3

You should know from saponification that NaOH cleaves ester bonds.

∴ Key is (A)

Question 4 Amides are essentially neutral. ∴ Key is (A)

Question 5

(a) At 25°C, $K_w = 1 \times 10^{-14}$

$\therefore [OH^-][H_3O^+] = 1 \times 10^{-14}$ $(K_w = [OH^-][H_3O^+])$

$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$

$\therefore n(H_3O^+) : n(OH^-) = 1:1 = [H_3O^+] : [OH^-]$ $(n \propto c)$

So, $[H_3O^+] = [OH^-]$

$\therefore [OH^-][OH^-] = 1 \times 10^{-14}$

$[OH^-] = \sqrt{1 \times 10^{-14}}$

$= 1.00 \times 10^{-7}$ M ①

(b) Let solubility be s mol L^{-1}.

$Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$ ①

$n(Fe^{3+}) : n(OH^-) : n(Fe(OH)_3) = 1:3:1$

$= [Fe^{3+}] : [OH^-] : [Fe(OH)_3]$ $(c \propto n)$

$\therefore [Fe^{3+}] = [Fe(OH)_3] = s$ M

$[OH^-] = [Fe(OH)_3] \times 3 = 3s$ M

In water, $[OH^-] = 1.00 \times 10^{-7}$ M already (part (a))

Since $K_{sp} = 2.0 \times 10^{-39}$,

assume $K_{sp} \ll 1.00$

$\therefore$ assume $[OH^-]$ due to $Fe(OH)_3$ is negligible compared to that due to water ①

So, $[OH^-]_{eq} = [OH^-]_{Fe(OH)_3} + [OH^-]_{H_2O}$

$= 1.00 \times 10^{-7} + 3s$

$\approx 1.00 \times 10^{-7}$ M

$K_{sp} = [Fe^{3+}][OH^-]^3$ ①

$2.0 \times 10^{-39} = (s)(1.00 \times 10^{-7})^3$

$s = \dfrac{2.0 \times 10^{-39}}{(1.00 \times 10^{-7})^3} = 2.0 \times 10^{-18}$ mol L^{-1}. ①

Question 6

You're meant to draw structural formulae but I cannot be bothered:

A:  (propan-1-ol)

B: $H-H$ (hydrogen gas)

C:  (but-2-ene)

D:  (but ane)

E:  (1° carbo cation)

① for each correct

Question 7

(a) For $PbSO_4$: $K_{sp} = [SO_4^{2-}][Pb^{2+}]$

$$\therefore [Pb^{2+}]_{precip} = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{2.53 \times 10^{-8}}{0.10} = 2.53 \times 10^{-7} M$$

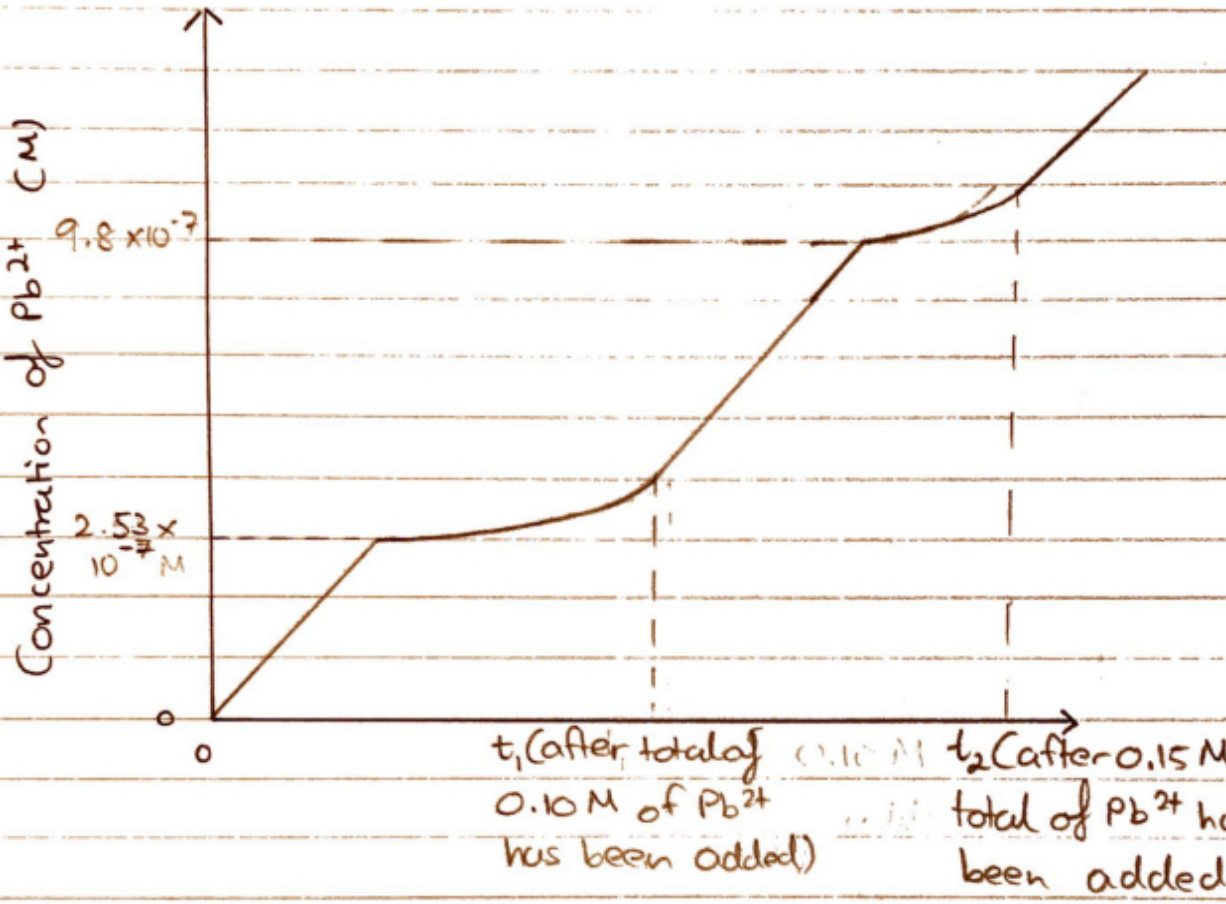
For PbI_2: $K_{sp} = [Pb^{2+}][I^-]^2$

$$[Pb^{2+}]_{precip} = \frac{K_{sp}}{[I^-]^2} = \frac{9.8 \times 10^{-9}}{0.1^2} = 9.8 \times 10^{-7} M$$

$\because 2.53 \times 10^{-7} M < 9.8 \times 10^{-7} M$, $PbSO_4$ will precipitate 1st

$\therefore$ precipitation at $2.53 \times 10^{-7} M$

(b)



-① for each of the following missing:

- values on y-axis
- values on x-axis (i.e. labels and descriptions of t_1, t_2)
- linear portions of graph
- curved portions of graph
- linear portions must be parallel
- curved portions <u>must</u> smoothly segue into next linear portion (i.e. instantaneous rate = pour rate).

Question 8

Consider the question instead as:

'15.00 mL of 0.1500 M NH_3 is titrated with 30.00 mL of 0.1000 M HCl'

$NH_{3(aq)} + HCl_{(aq)} \rightarrow NH_4Cl_{(aq)}$

$n(NH_3) : n(HCl) = 1:1$

∴ need equal moles of HCl and NH_3 for complete neutralisation

$c = \frac{n}{V} \Rightarrow n = Vc$

$n(HCl) = \frac{30.00}{1000} \times 0.1000$

$= 0.003$ mol

$n(NH_3) = \frac{15.00}{1000} \times 0.1500$

$= 0.00225$ mol

∵ $0.003 > 0.00225$ (mol)

∴ $n(HCl) > n(NH_3)$

∴ HCl in excess.

$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

$n(HCl) : n(H_3O^+) = 1:1$

∴ $n(H_3O^+) = n(HCl)_{excess}$

$= n(HCl)_{total} - n(NH_3)_{total}$

$= 0.003 - 0.00225$

$= 0.00075$ mol ①

$c = \frac{n}{V}$

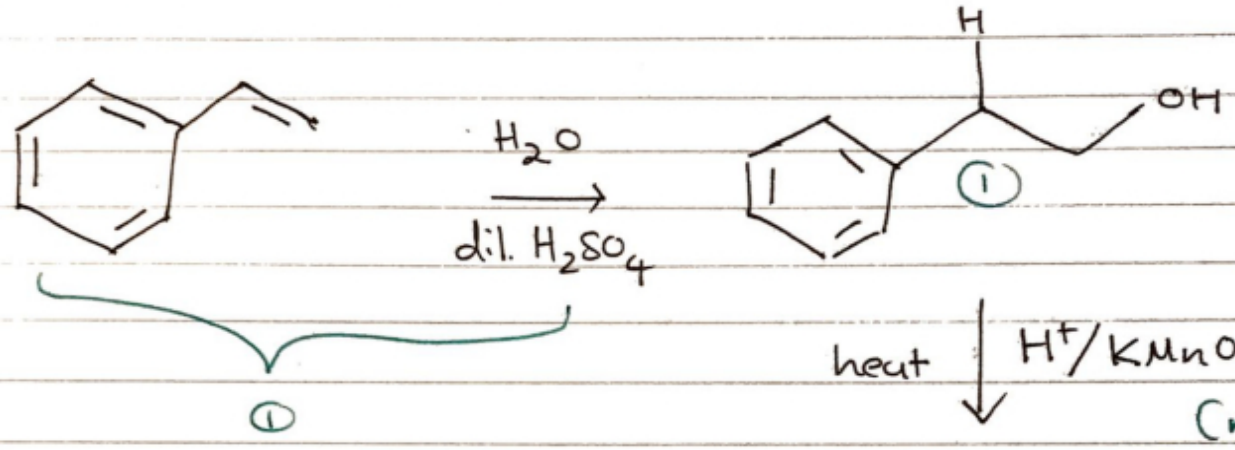
$[H_3O^+] = \frac{n(H_3O^+)}{V(HCl) + V(NH_3)} = \frac{0.00075}{\frac{30.00}{1000} + \frac{15.00}{1000}}$

$= 0.017$ M (2 s.f) ①

$pH = -\log_{10}[H_3O^+] = -\log_{10} 0.017$

$= 1.7782$ (4 d.p) ① (need correct decimal places)

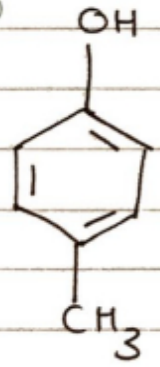
Question 9



Question 10

(a) 4 ①

(b)



① benzene ring
① methyl and hydroxyl groups
① correct structure

You do NOT need a proton NMR data sheet for this question. You should know that double bonds increase chemical shift.

Question 11

(a) R | $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$

I (M)	0.10	0	0
C (M)	$-x$	$+x$	$+x$
E (M)	$0.10 - x$	x	x

Since $K_c = 8.30 \times 10^{-4}$, assume $K_c \ll 1.00$

$\therefore$ assume $x \ll 0.10\,M$

$\therefore$ assume $[COCl_2]_{eq} = 0.10 - x \approx 0.10\,M$

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]} \quad (1)$$

$$8.30 \times 10^{-4} = \frac{(x)(x)}{0.10}$$

$$x = \sqrt{8.30 \times 10^{-4} \times 0.10}$$

$$= 9.1 \times 10^{-3}\,M$$

$= [CO]_{eq} = [Cl_2]_{eq}$ (1)

For $[COCl_2]$, you may give: 0.10 M (as per assumption)

OR $0.10 - 9.1 \times 10^{-3} = 0.091\,M$ (2 s.f.) (1)

Normally, when small x assumption is invalid (as in this case), you would have to solve by ~~Fail~~ iteration which is NOT in the syllabus.

(b) Yes (1)

(c) Using idea from part (b), the equilibrium position of 0.15 M CO and 0.25 M Cl_2 is the same as that of

0.15 M $COCl_2$, 0.00 M CO, 0.10 M Cl_2 (react completely to left) (1)

This allows us to use small x assumption:

	$COCl_2(g)$	$\rightleftharpoons$	$CO(g)$	+	$Cl_2(g)$
I (M)	0.15		0.00		0.10
C (M)	$-x$		$+x$		$+x$
E (M)	$0.15-x$		x		$0.10+x$

assume $K_c = 8.3\times10^{-4} \ll 1.0$ (1) (justify assumption)

$\therefore$ assume $x \ll 0.10 < 0.15$

i.e. $[COCl_2]_{eq} = 0.15 - x \approx 0.15\,M$ (1) ($[COCl_2]_{eq}$ and $[Cl_2]_{eq}$)

and $[Cl_2]_{eq} = 0.10 + x \approx 0.10\,M$

$$K_c = \frac{[CO][Cl_2]}{[COCl_2]}$$ (1)

$$8.3\times10^{-4} = \frac{(x)(0.10)}{0.15}$$

$$x = \frac{0.15}{0.10} \times 8.3\times10^{-4} = 0.0012\,M\ (2\,s.f.)$$

$= [CO]_{eq}$ (1), $[COCl_2]_{eq} = 0.15\,M$ and $[Cl_2]_{eq} = 0.10\,M$

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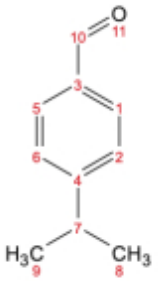

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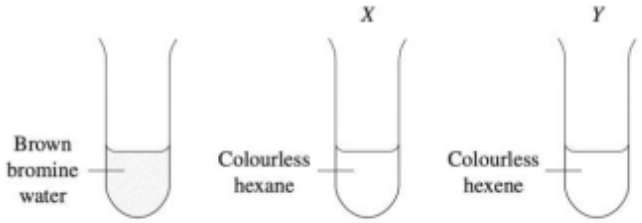

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