Answers (Prelim 2 H2 Paper 2)

For Examiner's Use

Answer ALL questions on the spaces provided.

1 You are given a number of different acids to investigate how the enthalpy change of neutralisation, $\Delta H_{neutralisation}$, varies when the acids are neutralised with aqueous sodium hydroxide, NaOH.

(a) **(i)** Hydrochloric acid, nitric acid and sulfuric acid are all strong acids.

Predict how $\Delta H_{neutralisation}$ values for these acids would compare with each other.

The three acids should have the same ΔH_{neut} values. Since all strong acids dissociate fully in water and ΔHneutralisation is when one mole of water is produced during acid-base reaction.

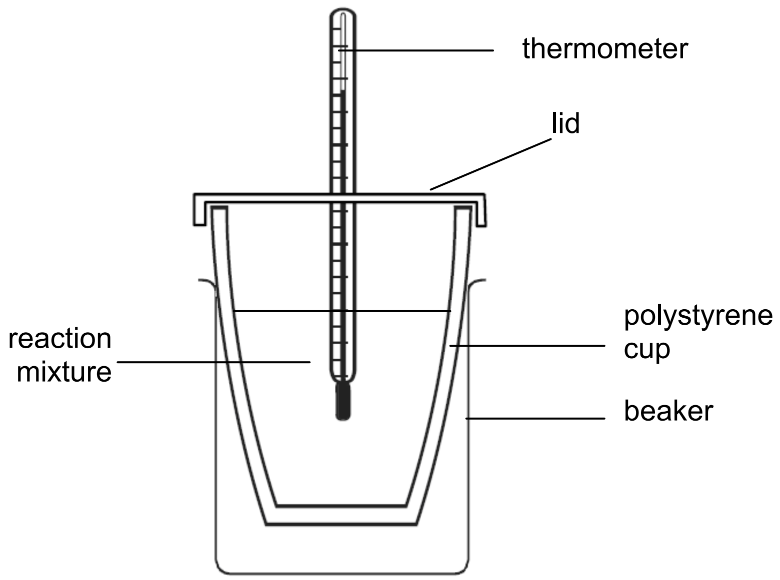
(ii) Predict and explain how the expected $\Delta H_{neutralisation}$ for a weak acid, such as ethanoic acid or ethanedioic acid, compares with that for hydrochloric acid.

[2]

ΔH_{neut} for a weak acid should be less exothermic (ΔH is more positive or less negative) than a strong acid because some of the energy is absorbed when the weak acid dissociates into ions.

(b) **(i)** Draw and label a diagram of the apparatus you would use to determine the temperature change, ΔT, when each of the acids reacts with 30.0 cm^3 of 2.0 mol dm^{-3} aqueous sodium hydroxide.

Any experimental method that is normally carried out in a college laboratory may be used.



(ii) Identify **one** possible source of error in the experiment and state how you would minimise the effect. [3]

S/N	Source of error	Improvement
1	Heat is lost to the surroundings.	Use wind-shield. (If a lid is not used in the set-up above, a lid can be used to cover the cup to reduce heat loss (due to convection). (If a beaker is not used in the set-up above, a beaker can be used to contain the cup to reduce heat loss (due to convection).)
2	The thermometer used may be of low precision.	Use a more precise thermometer to allow temperature to be read to a greater degree of precision.
3	There could be some loss of material if the solution overflows or sprays out.	Use a larger cup/container. (If a lid is not used in the set-up above, a lid can be used to minimise spray.)

(c) In each experiment, 30.0 cm^3 of 2.0 mol dm^{-3} aqueous NaOH is to be used. Suggest appropriate volumes for each of the acids to be used in the individual experiments. [1]

Ans

Acid		Volume/ cm^3	Concentration/ mol dm^{-3}
Hydrochloric	HCl	30	2.0
Ethanedioic	$(CO_2H)_2$	15	1.0

(d) Ethanedioic acid is a hydrated crystalline solid, $(CO_2H)_2.2H_2O$.

Outline how you would prepare 100 cm^3 of 1 mol dm^{-3} solution of ethanedioic acid. In your answer, you should show how you determine the initial mass of ethanedioic acid to be used. [*A*r: C, 12.0; H, 1.0; O, 16.0]

[You are given more writing space on the following page]

No. of moles of ethanedioic acid = 100/1000 x 1 = 0.1 moles
Mass = 0.1 x [2(12.0) + 4(16.0) + 2 (1.0) + 2 (18.0)] = 12.6g

(i) Measure the mass of an empty weighing bottle.
(ii) Measure 12.60 g of the ethanedioic acid into the weighing bottle.
(iii) Transfer the sample into a 100cm^3 beaker.
(iv) Dissolve the solid with less than 100 cm^3 of distilled water (in beaker) and transfer to a 100cm^3 volumetric flask along with the rinsings.
(iii) top up with distilled water to 100 cm^3 mark
(iv) Inversion/shaking/swirling of flask to mix the solution

[4]

(e) Using the volume and concentration from **(c)** and ΔT to represent the temperature change, derive a mathematical expression for the enthalpy change of neutralisation

of sodium hydroxide with hydrochloric acid.
[4.3 J of heat energy raise the temperature of 1 cm^3 of any solution by 1 °C]

[1]

$\Delta H_{neutralisation} = -\dfrac{\text{(vol of HC}l\text{ + vol of NaOH)} \times \text{temp rise} \times 4.3}{\text{moles of water formed}}$

$= -\dfrac{(30+30)\times 4.3\times \Delta T}{30\times 10^{-3}\times 2} = \underline{-4300\ \Delta T}$

(f) Suggest what modification you could make to your experimental procedure to ensure **complete neutralisation** of the acid.

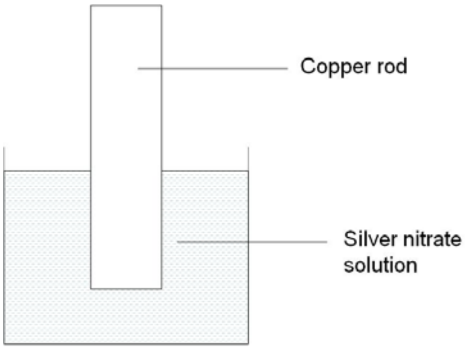
[1]

The number of moles of acid used can be made slightly lesser than the no of moles of NaOH used so that the acid is the limiting reagent.

[Total: 12]

2 *The use of the Data Booklet is relevant to this question.*

(a) The diagram below shows an experimental setup when a copper rod is dipped into a silver nitrate solution. After one hour, the copper rod is coated with a shiny substance and the solution turned slightly blue.



(i) Write an **ionic** equation, with state symbols, for the reaction that has occurred.

$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

(ii) Given that $\Delta G^\theta = -nFE^\theta$, where n is the number of moles of electrons transferred in the reaction, and E^θ is the electromotive force generated, calculate ΔG^θ, in kJ mol^{-1}, of the above reaction at standard conditions.

$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$ $E^\theta = +0.34V$
$Ag^+(aq) + e \rightleftharpoons Ag(s)$ $E^\theta = +0.80V$
$E^\theta = +0.80 - (+0.34)$
$= +0.46V$

$\Delta G^\theta = -nFE^\theta$
$= -2 \times 96500 \times 0.46$
$=$ **−88.8** kJ mol^{-1} (spontaneous)

(iii) Suggest and explain if the above reaction has a positive or negative ΔS^θ.
As the number of free aqueous ions is reduced, the system will be less disordered. The sign of ΔS^θ should be negative.

[4]

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(b) In the laboratory, there are three bottles labelled **N**, **P** and **Q**. Each bottle contains one of the following reagents:

Cl_2(aq), NaI(aq) and KBr(aq)

Three tests were carried out using the reagents in the bottles. The results are summarised in the table below:

Test	Procedure	Observations
1	Mix reagent in bottle **N** with reagent in bottle **P**	No Change
2	Mix reagent in bottle **N** with reagent in bottle **Q**	Mixture turn brown
3	Mix reagent in bottle **P** with reagent in bottle **Q**	Mixture turn brown

(i) Deduce and explain which bottle contains Cl_2(aq). Write chemical equations with state symbols to support your reasoning.

Bottle **Q** contains Cl_2 (aq) which oxidized / displaced Br^- (aq) to Br_2 (aq) and I^- (aq) to I_2 (aq) which accounts for the brown mixture obtained.

$$Cl_2\,(aq) + 2Br^-\,(aq) \rightarrow 2Cl^-\,(aq) + Br_2\,(aq)$$

$$Cl_2\,(aq) + 2I^-\,(aq) \rightarrow 2Cl^-\,(aq) + I_2\,(aq)$$

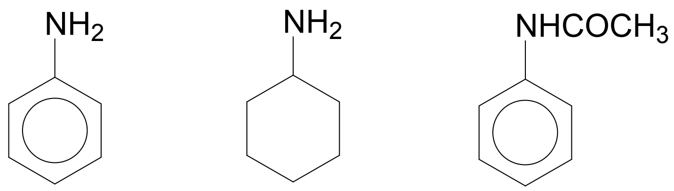
(ii) To determine which bottle contains NaI(aq) and KBr(aq) respectively, tests 2 and 3 were repeated. Hexane was added to the resulting reaction mixture after the tests were conducted. The bottles were then shaken and allowed to stand.

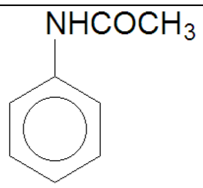
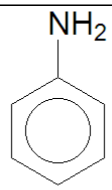
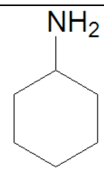
State the observations which will help to identify which bottle contains NaI(aq) and KBr(aq) respectively.

The bottle with reddish brown organic layer contains KBr (aq) initially.
The bottle with violet / purple organic layer contains NaI (aq) initially.

[5]

(c) Arrange the following compounds in order of decreasing pK_b, giving reasons for your answer.



		
Highest pK_b	$\longrightarrow$	Lowest pK_b

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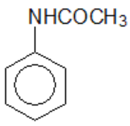
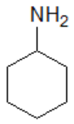
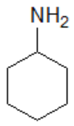
For  , the lone pair of electrons on N atom is delocalized over the carbonyl group and is not available to accept a proton. Hence it is neutral and least basic among the three compounds.

Phenylamine is less basic than  as the lone pair on N atom is delocalized into the benzene ring and is thus less available to accept a proton.

OR

 is the most basic as the alkyl group increases the electron density on the N atom, making the lone pair of electrons more available to accept a proton[½m] than in ammonia.

[3]

(d) Magnesium hydroxide is an inorganic compound with the chemical formula $Mg(OH)_2$. A suspension of $Mg(OH)_2$ in water is often called 'milk of magnesia' because of its milk-like appearance. It is commonly used in laxatives.

(i) Write an expression for the K_{sp} of $Mg(OH)_2$.

$K_{sp} = [Mg^{2+}(aq)]\ [(OH)^{-}(aq)]^2$

(ii) Calculate the concentration of $Mg^{2+}(aq)$ in a saturated solution of $Mg(OH)_2$, given that the pH of the solution is 9.25. You are given that K_{sp} of $Mg(OH)_2$ is 1.8×10^{-12} $mol^3\ dm^{-9}$.

pH=9.25

pOH= 4.75,
$[(OH)^{-}(aq)] = 1.78 \times 10^{-5}$ mol dm^{-3}

$K_{sp} = [Mg^{2+}(aq)]\ [(OH)^{-}(aq)]^2$

$[Mg^{2+}(aq)] = 1.8 \times 10^{-12} / (1.78 \times 10^{-5})^2 = \underline{5.68 \times 10^{-3}\ mol\ dm^{-3}}$

[3]

[Total: 15]

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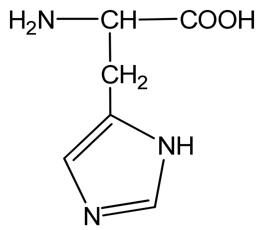
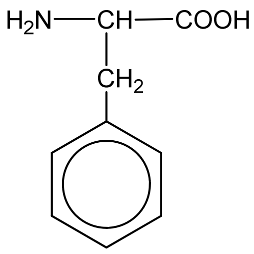
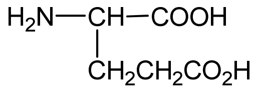
3 **(a)** Keratin is a fibrous protein found in fingernails. A tripeptide, his-phe-glu, obtained from Keratin was further hydrolysed to obtain the individual amino acids.

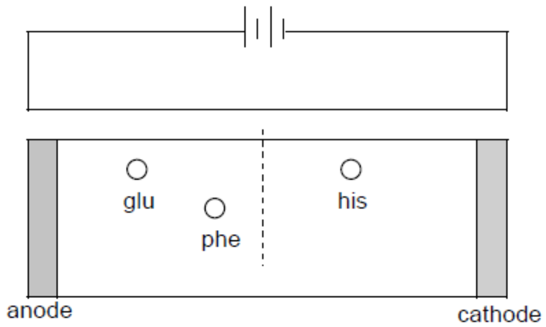
Amino Acid			
	his	phe	glu
Isoelectric point	7.58	5.48	3.10

The individual amino acids were added to a buffer solution of pH 6.5 and placed at the centre of the gel electrophoresis plate. A potential difference was then applied across the plate.

(i) Indicate the relative positions of the amino acids on the diagram below. In your answer, use the labels "○**his**", "○**phe**" and "○**glu**" to represent the amino acids his, phe and glu respectively.

[2]

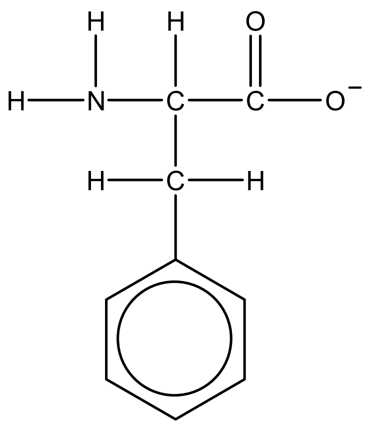
Answer:



(ii) Draw the displayed formula of phe in the buffer solution at pH 6.5.

[1]

Answer:



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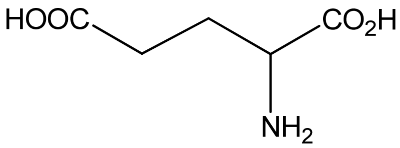
Answers (Prelim 2 H2 Paper 2)

(b) Explain why precipitation is seen when drops of dilute acid are added to Keratin. [2]

Denaturation has occurred. Adding H^+ protonates the ionic R groups and this disrupts the ionic interactions/electrostatic attractions, disrupting the tertiary and quaternary structures of the protein.

(c) The formation of GABA, an inhibitory neurotransmitter in the brain and retina, comes from the metabolism of glutamic acid.



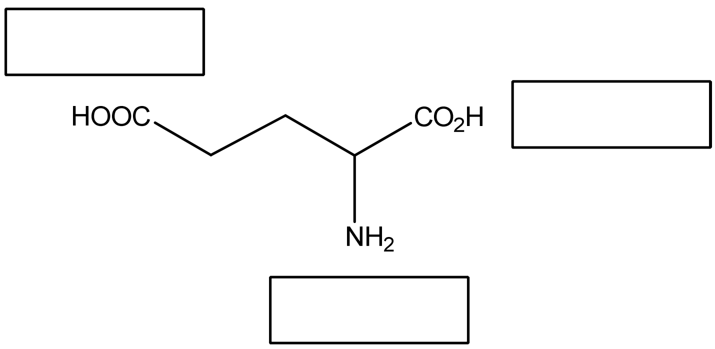
glutamic acid

(i) Explain what is meant by the term pK_a as applied to a weak acid HA. [1]

$pK_a = -\log K_a$ where K_a is the acid dissociation constant of weak acid.

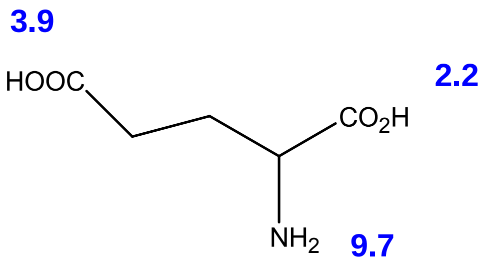
(ii) There are three pK_a values associated with glutamic acid: 2.2, 3.9 and 9.7.

Assign the pK_a values to the appropriate functional groups present in glutamic acid.



[1]

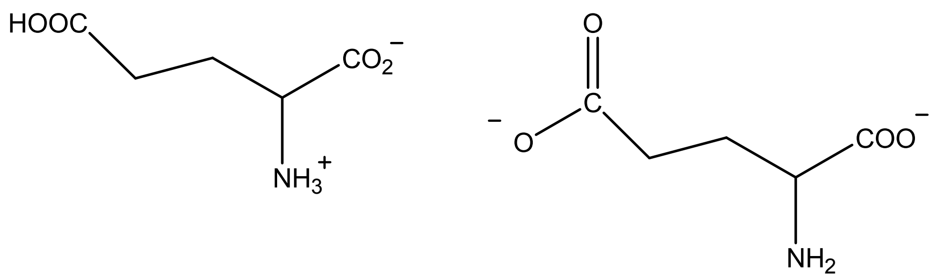
Answer:



(iii) Make use of these pK_a values to suggest the major species present in solutions of glutamic acid with the following pH values. [2]

pH=3 pH=11

Answers (Prelim 2 H2 Paper 2)



(iv) Compound **R** can be used as a precursor of GABA.

$HO_2C–CH_2CH_2CH_2OH$

R

Both glutamic acid and **R** have similar relative molecular masses. Based on melting point analysis, it was found that glutamic acid has a much higher melting point than **R**. Explain the difference in their melting points. [3]

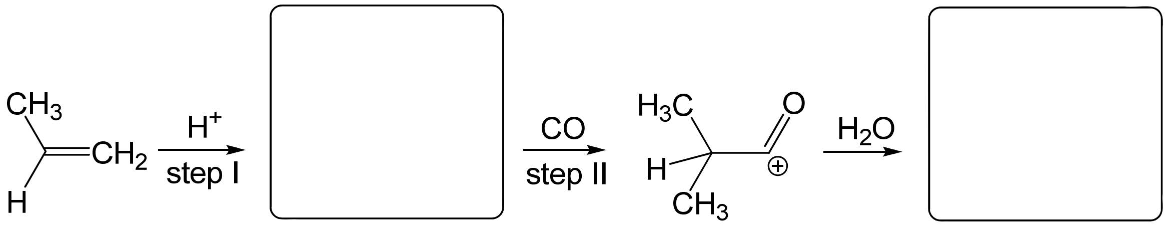
Glutamic acid exists as zwitterions in a giant ionic structure with strong electrostatic forces of attraction between the zwitterions.

W has a simple molecular structure with hydrogen bonds between its molecules. The strong electrostatic forces in glutamic acid are much stronger than the hydrogen bonds in W. Thus, a larger amount of energy is needed.

[Total: 12]

4 Alkenes are very reactive due to the presence of unsaturation.

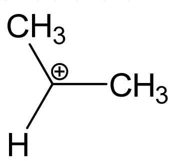
In the Koch reaction, alkenes can react with carbon monoxide and water to form carboxylic acids. The reaction scheme below shows propene undergoing the Koch reaction.



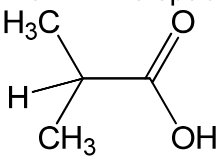
carbocation intermediate

final organic product

(a) **(i)** Alkenes undergo electrophilic addition in the presence of electrophiles such as H^+ due to the electron-rich π bond. Draw in the space provided above, the structure of the carbocation intermediate formed from propene.



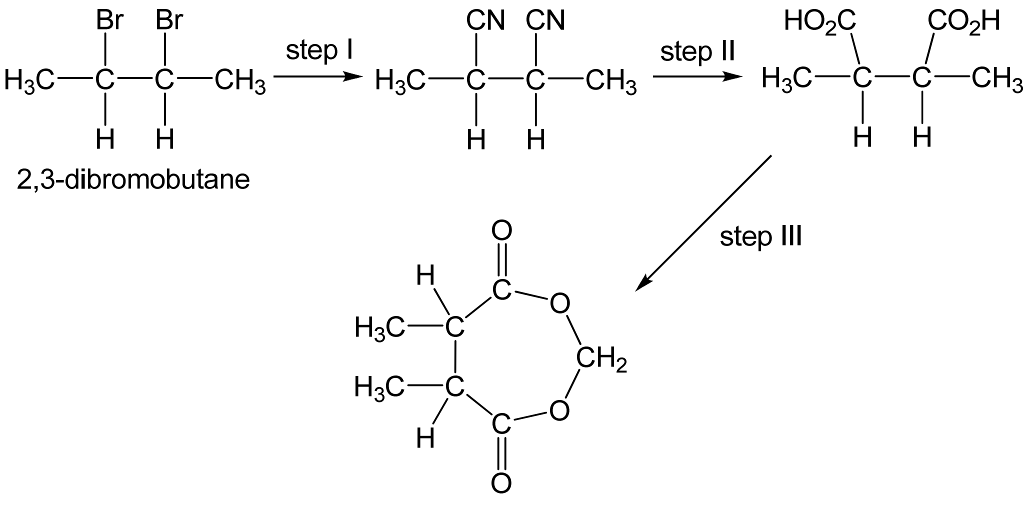
(ii) Draw in the space provided above, the structure of the final organic product.



[2]

(b) **(i)** The reaction scheme below shows a three-step synthetic route to synthesise a dicarboxylic acid from 2,3-bromobutane, the product of which can react with a diol to form compound **S**, a cyclic diester.

Suggest the reagents and conditions at each step of the reaction.



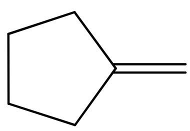
S

Step I:
Reagent(s): ethanolic KCN
Condition(s): Heat with reflux

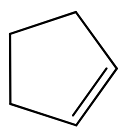
Step II:
Reagent(s): dilute HC*l*/H_2SO_4/HNO_3
Condition(s): Heat with reflux

Step III:
Reagent(s): $CH_2(OH)_2$
Condition(s): trace amount of concentrated H_2SO_4
heat with reflux

(ii) Suggest a simple chemical test you would use to distinguish between the two types of alkenes shown below.



methylenecyclopentane



cyclopentene

Answers (Prelim 2 H2 Paper 2)

Reagent(s): $KMnO_4$
Condition(s): dilute H_2SO_4, heat
Observation for methylenecyclopentane: Purple $KMnO_4$ decolourises , effervescence observed, gas evolved forms white ppt with $Ca(OH)_2$ (aq)
Observation for cyclopentene: Purple $KMnO_4$ decolourises, no effervescence observed

[7]
[Total: 9]

5 Hydrogen reacts with nitrogen monoxide to give nitrogen and steam as shown in the following equation.

$$2NO(g) + 2H_2(g) \longrightarrow N_2\square(g) + 2H_2O(g)$$

The following mechanism was proposed for the reaction between NO(g) and H_2(g).

Step I	$2NO \rightleftharpoons N_2O_2$	*fast*
Step II	$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$	*slow*
Step III	$N_2O + H_2 \longrightarrow N_2 + H_2O$	*fast*

(a) **(i)** Draw dot-and-cross diagrams to show the electronic structures of NO and N_2O_2. Use your diagrams to explain why step I is a likely first step.

NO has an unpaired electron / single electron and so, is reactive and can combine/dimerise readily to form N_2O_2.

(ii) The following kinetic experiments were carried out and the data recorded as shown below.

Experiment	Concentration / mol dm^{-3}		Initial rate / mol dm^{-3} s^{-1}
	NO (g)	H_2 (g)	
1	0.001	0.1	7.00×10^{-4}
2	0.001	0.2	1.40×10^{-3}
3	0.003	0.2	1.26×10^{-2}

Using these data, state the order of reaction with respect to NO and H_2 and write the rate equation for the reaction.

Order of reaction with respect to NO: **2**

Order of reaction with respect to H_2: **1**
Rate = k $[H_2]$ $[NO]^2$

(iii) With reference to the above mechanism, prove that the rate equation you have derived in **a(ii)** is correct.

Rate $= k' [N_2O_2] [H_2]$
$= k' \mathbf{(k'' [NO]^2)} [H_2]$ since $[N_2O_2] \propto [NO]^2$
$= k [H_2] [NO]^2$ where $k = k'k''$

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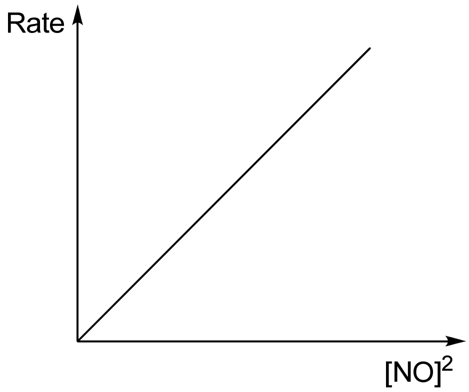
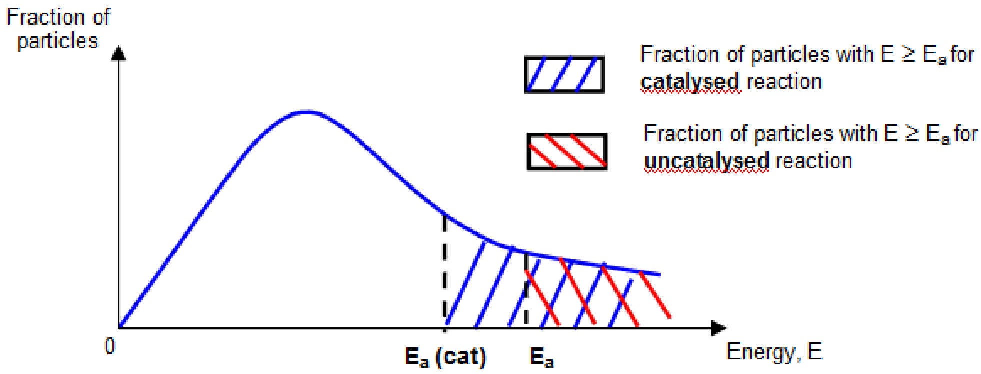
(iv) Sketch the graph of rate against $[NO]^2$.



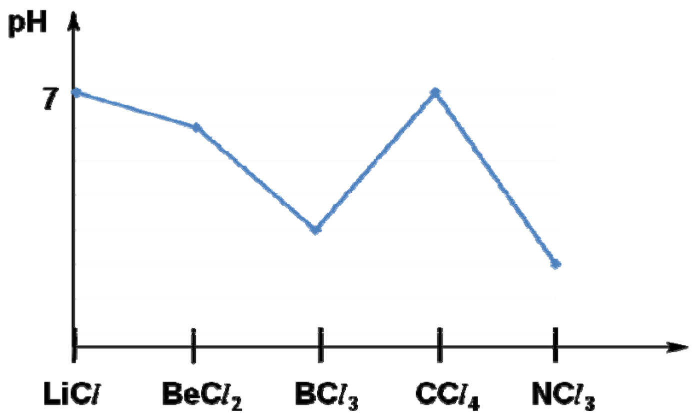
(v) Explain, with the aid of a Maxwell-Boltzmann distribution curve, why the addition of a catalyst speeds up the rate of a chemical reaction.



- The catalyst provides an alternative pathway with a lower activation energy, E_a(cat)
- Fraction of particles with energy equal to or greater than the activation energy, E_a increases.
- Frequency of effective collisions taking place in the reaction increases.
- Since rate of reaction is proportional to the frequency of effective collisions, rate of reaction increases.

[11]

(b) (i) The chlorides of Period 2 elements behave *similarly* to Period 3 elements. Based on your knowledge of Period 3 elements, sketch a graph of pH against the chlorides of lithium to nitrogen. In particular, the chloride of carbon forms an oily layer when mixed with water.



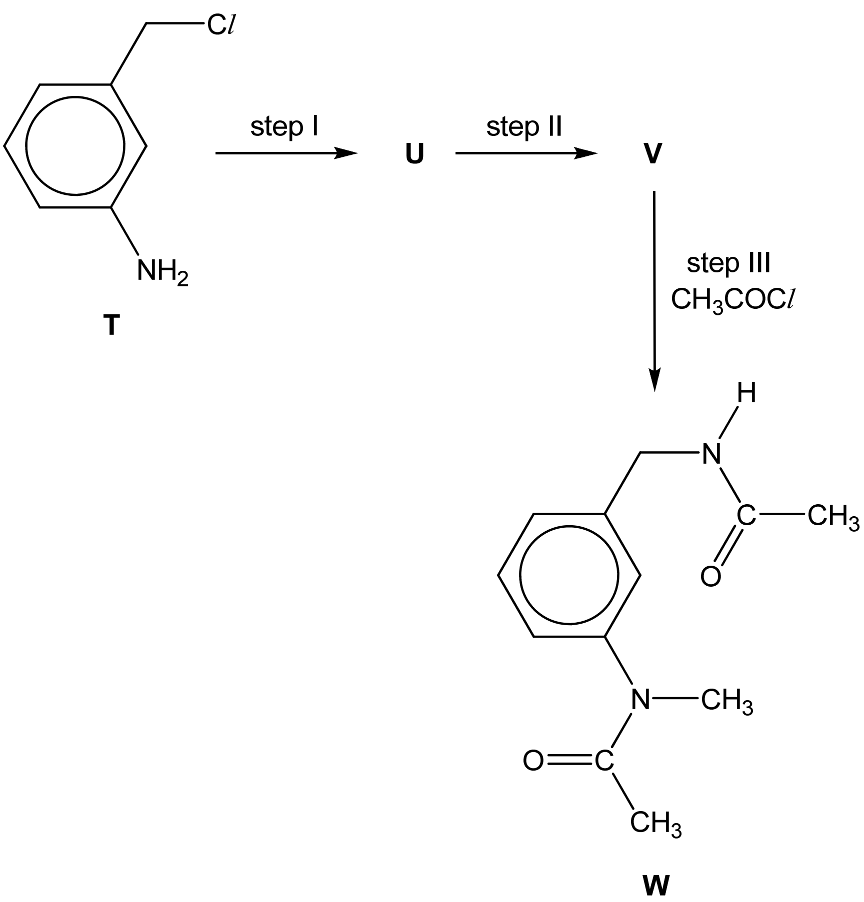
(ii) Write an equation with state symbols to account for the pH value of NCl_3 when dissolved in water. Aqueous HNO_2 is formed in the process.

$NCl_3(l) + 2H_2O(l) \rightarrow HNO_2(aq) + 3HCl(g)$

[2]

[Total: 13]

6 (a) Compound **W** can be synthesised from compound **T** via a series of steps.



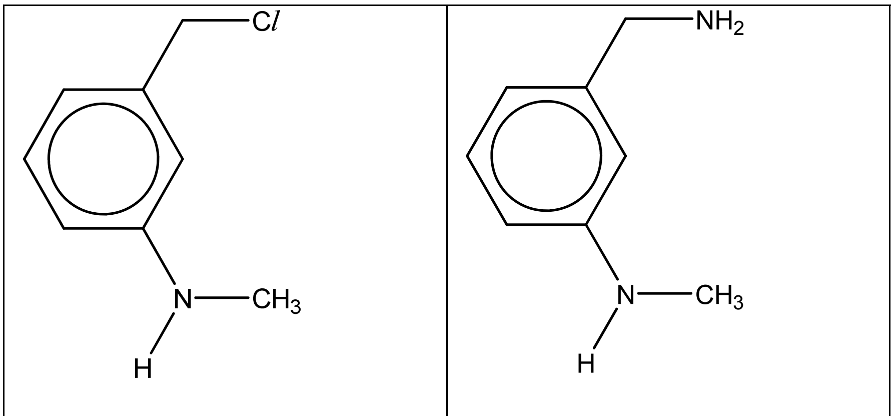
(i) State the reagents and conditions for step I and step II.

Answers (Prelim 2 H2 Paper 2)

Step I
Reagent(s): limited CH_3Cl
Condition(s): heat with reflux

Step II
Reagent(s): excess ammonia
Condition(s): ethanol, heat in sealed tube

(ii) Draw the structures of compound **U** and **V** in the boxes below.



Compound **U** | Compound **V**

(iii) All 3 steps are the same type of reaction. State the type of reaction for step I to step III.

Nucleophilic substitution

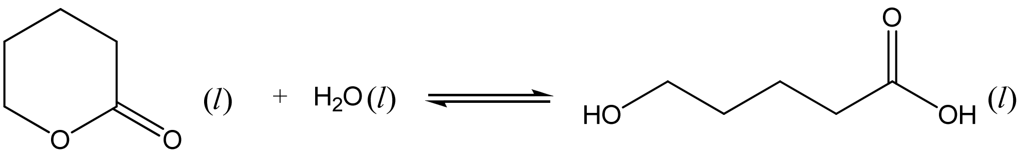
(iv) A student incorrectly claimed that 5 g of Compound **V** will only require 2 m*l* of CH_3COCl to react completely. Determine the correct volume of CH_3COCl needed for the reaction.

You are given the following information:
M_r of Compound **V** = 136.0
Density of CH_3COCl = 1.104 g/m*l*

No. of moles of Compound **V**= 5/136 = 3.676×10^{-2}
No. of moles of CH_3COCl required = $3.676 \times 10^{-2} \times 2 = 7.352 \times 10^{-2}$
Mass of CH_3COCl required = $7.352 \times 10^{-2} \times (12 \times 2+3+16+35.5)$
= 5.772g
Volume of CH_3COCl = 5.772/1.104 = 5.23 m*l*

[7]

(b) 5-hydroxypentanoic acid is the product of the following hydrolysis, which exists in a *dynamic equilibrium*.



tetrahydro-2*H*-pyran-2-one   5-hydroxypentanoic acid

Answers (Prelim 2 H2 Paper 2)

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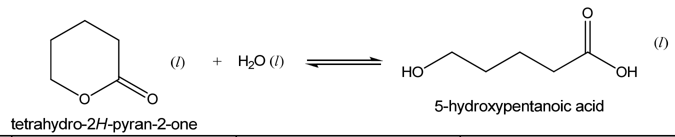
(i) Explain what is meant by the term *dynamic equilibrium*.

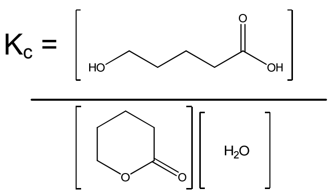
A system is said to be in dynamic equilibrium when the rate of forward reaction is equal to the rate of backward reaction and the concentration of the reactants and products remains unchanged.

(ii) In an experiment, 2.0 mol of tetrahydro-2*H*-pyran-2one was allowed to undergo hydrolysis.

Given that 95% of tetrahydro-2*H*-pyran-2one remained at equilibrium and the total volume of the mixture remained constant at 2 dm^3, calculate the K_c for this reaction. You can assume that $[H_2O]$ = 55.5 mol dm^{-3} throughout.



Initial no. of moles	2.0	111	0
Change in moles	-(0.05X2.0)= -0.1	0	+0.1
Equilibrium no. of moles	1.9	111	0.1
Equilibrium concentration	1.9/2 = 0.95	55.5	0.1/2 = 0.05



$$K_c = \frac{\left(\frac{0.10}{2}\right)}{55.5\left(\frac{1.90}{2}\right)} = 9.48 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3$$

[4]

[Total: 11]