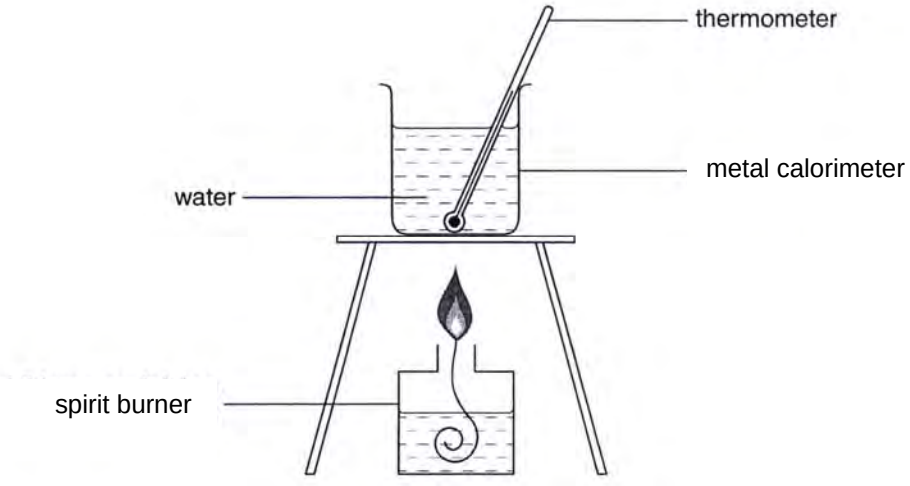
Victoria Junior College
2013 H2 Chemistry Prelim Exam 9647/2
Suggested Answers

1 Planning

A student was provided with a spirit burner containing a 'fuel mixture' which was prepared by mixing equimolar amounts of hexane and ethanol. The enthalpy change of combustion of this 'fuel mixture' is −13.2 kJ per mole of 'fuel mixture'. He was told to use the enthalpy change of combustion of this 'fuel mixture' to find the heat capacity of a metal calorimeter using the apparatus shown below. Heat capacity is defined as the number of joules of heat needed to raise the temperature of the calorimeter by one Kelvin or one degree Celsius.



Additional information: Specific capacity of water is 4.2 J cm^{-3} K^{-1}

(a) Construct a balanced equation for the complete combustion of the 'fuel mixture' with state symbols.

$C_6H_{14}(l)$ + $C_2H_5OH(l)$ + 25/2 $O_2(g)$ → $8CO_2(g)$ + $10H_2O(l)$

[1]

(b) Identify two possible sources of error and suggest an improvement to overcome each of them in the experiment.

Errors:
Heat loss to the surroundings by the calorimeter and water.
Loss in amount of fuel mixture due to evaporation of the fuel mixture as ethanol and hexane are volatile liquids.

Improvements:
Cover and lag the calorimeter with non-flammable insulating material and conduct the experiment in a draught-free room, to minimize heat loss by the calorimeter and water to the surroundings.
Cover the spirit burner to minimize rate of evaporation so as to minimize loss of fuel mixture.

[3]

(c) Write a plan to determine the heat capacity of the metal calorimeter using the apparatus provided.
In your plan you should give details of the procedure (number your steps) and provide a table to record the readings to be taken, including the units.

1) Weigh the spirit burner containing the 'fuel mixture'
2) Using a measuring cylinder, measure 100 cm^3 of water into the metal calorimeter.
3) Measure the initial temperature of the water using a thermometer.
4) Light the burner and allow it to heat the water in the calorimeter.
5) Monitor the temperature of water using the thermometer, and extinguish the flame when the temperature of the water reaches about 5 ^oC
6) Measure the final temperature of the water.
7) Cool and reweigh the spirit burner with the remaining 'fuel mixture'.

Initial temperature of water/ ^oC	**T_1**
Final temperature of water/ ^oC	**T_2**
Initial mass of spirit burner with 'fuel mixture' / g	**M**
Final mass of spirit burner with remaining 'fuel mixture' /g	**N**

[5]

(d) Outline how you would determine the heat capacity of the metal calorimeter based on the plan that you have written and other information given in this question.

Since density of water is 1 g cm^{-3}, mass of the water in the calorimeter = 100 g

Let the Heat capacity of the calorimeter be C J $^oC^{-1}$

Temperature rise of the water in the calorimeter = (T_2 – T_1) = T ^oC
Heat gained by water and calorimeter
= 100 x 4.2 x T + C x T = (420 + C)T J

Mass of 'fuel mixture' burned = (M-N) g = P g
Molar mass of 'fuel mixture' = 86 + 46 = 132 g mol^{-1}
Hence, amount of 'fuel mixture' = P/132 mol

Heat lost by 'fuel mixture' = 13200 x P/132 = 100P J

Heat lost by 'fuel mixture' = Heat gained by water and calorimeter
100P = (420 + C)T
C = 100P/ T – 420

[3]

[Total: 12]

2 (a) World War I is sometimes known as 'the Chemists' War'. Knowledge of chemistry was applied towards developing high explosives and new methods of warfare such as the large scale use of poison gas.

The first successful use of chlorine as a poison gas was at Ypres, Belgium, on 22 April 1915. 170 tonnes (1 tonne = 1000 kg) of chlorine contained in 5730 cylinders was released forming a grey-green cloud which drifted across French troops. Chlorine can damage the eyes, nose, throat and lungs and is fatal at concentrations of 1000 ppm and above (1 ppm = 1 mg dm^{-3}). Early counter-measures to chlorine included instructing troops to cover their mouths with gauze pads soaked in sodium hydrogen carbonate solution. Eventually, more effective counter-measures to chlorine were developed and thus other poison gases were introduced.

(i) Calculate the maximum amount of chlorine gas that could have been released from one of the cylinders that was used at Ypres on 22 April 1915.

Amount of Cl_2 in 1 cylinder = $\frac{170000000}{71.0}$ **/ 5730 = 4.18 x 10^2 mol**

(ii) Determine the concentration of chlorine gas, in mol dm^{-3}, at 1000 ppm.

Concentration of Cl_2 in g dm^{-3} in 1000 ppm = $1000 \times \frac{1\ mg}{dm^3} \times \frac{1\ g}{1000\ mg}$ **= 1.00**

Concentration of Cl_2 in mol dm^{-3} = $\frac{1}{71.0}$ **= 0.0141 mol dm^{-3}**

(iii) In an accident, the chlorine gas from one such cylinder was released into a factory room of volume 25.0 m^3.
Determine if the concentration of chlorine gas was fatal. Assume that the gas was released at room temperature and pressure.

Volume of factory room = $25\ m^3 \times \frac{1\ dm^3}{1 \times 10^{-3}\ m^3}$ **= 25 000 dm^3**

Conc. of Cl_2 in the factory = $\frac{4.18 \times 10^2}{25000}$

= 0.0167 mol dm^{-3}

Since 0.0167 mol dm^{-3} > 0.0141 mol dm^{-3}, it is fatal.

[4]

(b) Hydrogen halides are dissociated at high temperatures according to the following equation:

$$2HX(g) \rightleftharpoons H_2(g) + X_2(g)$$

The approximate K_c values for the above equilibrium at various temperatures for the respective hydrogen halides are shown in the table:

Temperature / ^{o}C	K_c values for dissociation of HX		
	HC*l*	HBr	HI
800	10^{-13}	10^{-9}	10^{-5}
1000	10^{-10}	10^{-7}	10^{-4}
1200	10^{-9}	10^{-5}	10^{-3}
1400	10^{-7}	10^{-4}	10^{-2}

Using the above information and relevant data from the *Data Booklet*, describe and explain the relative thermal stability of the hydrogen halides.

From the table, it is observed that at each temperature, order of K_c is HI > HBr > HC*l*.
Since the larger the K_c values, the higher the degree of dissociation of HX, the order of degree of dissociation is HI > HBr > HC*l*.
From the Data Booklet, it is observed that order of bond energy is HC*l* > HBr > HI as shown:

	H – C*l*	H – Br	H – I
bond energy (kJ mol^{-1})	431	366	299

H–X bond energy decreases from HC*l* to HI due to increasing atomic size of X atom leading to decreasing H–X bond strength as degree of effective overlap between H and X atoms decreases from C*l* to I.
The H–I bond thus requires the least amount of energy to break, causing HI to be least thermally stable followed by HBr and then HC*l*.
Hence, order of thermal stability is HC*l* > HBr > HI.

[3]

(c) Aqueous solutions of HC*l*, HBr and HI (approximately 1 mol dm^{-3}) are almost completely ionised, but solutions in concentrated ethanoic acid are ionised to approximately 5, 20 and 50% respectively. Explain the phenomenon.

It can be deduced that CH_3CO_2H is a weaker base than H_2O and is less likely to accept H^+ from HX. Thus dissociation of HX occurs to a lesser extent in CH_3CO_2H. The reason is because bond energy decreases from HCl to HI, as atomic radius of halogen increases, causing acid strength to increase from HCl to HI, as seen from increase in %ionisation.

[2]

By comparison with the reactions of sodium halides with concentrated H_2SO_4, account for the behaviour of NaC*l*(s), NaBr(s) and NaI(s) when heated with the following concentrated acids:

(d) **(i)** with phosphoric(V) acid, H_3PO_4, all give the hydrogen halide in good yield.

H_3PO_4, unlike H_2SO_4, is a non-oxidising acid, and a stronger acid than HX, thus undergoes acid-base reaction with X^- to form HX.

(ii) with selenic(VI) acid, H_2SeO_4, all are converted into the free halogens.

H_2SeO_4 is a stronger oxidising agent than H_2SO_4, capable of oxidizing HX to X_2 (X = Cl, Br and I), unlike H_2SO_4, which cannot oxidise HCl to Cl_2.

(iii) with telluric(VI) acid, H_6TeO_6, there is no reaction.

H_6TeO_6 is a weaker acid than HX, thus unable to displace HX from X^- salt. It is a weaker oxidising agent than H_2SO_4, thus unable to oxidise HX to X_2.

[3]

(e) When chlorine is bubbled through a concentrated aqueous solution of ammonium chloride, a yellow oily liquid, nitrogen trichloride, is formed together with a solution of hydrochloric acid. A pungent gas together with a solution of sodium chlorate(I) is obtained when nitrogen trichloride is added to aqueous sodium hydroxide.

(i) Write balanced equations for the formation of nitrogen trichloride and its reaction with sodium hydroxide.

$3Cl_2 + NH_4Cl \rightarrow NCl_3 + 4HCl$
$NCl_3 + 3NaOH \rightarrow NH_3 + 3NaClO$

(ii) Sodium chlorate(I) can be produced using another method. Write a balanced equation for its production.

$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$

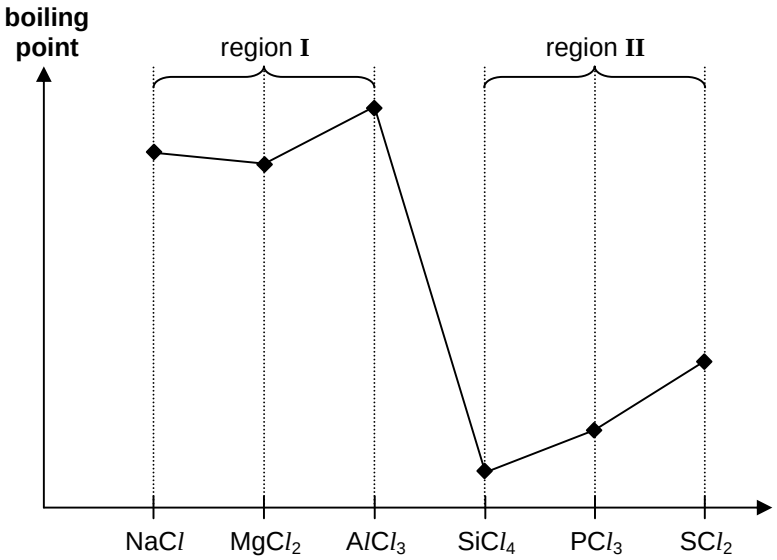
(iii) Give one domestic use for sodium chlorate(I).

It is used in the manufacture of household bleaches for whitening clothes.

[3]

[Total: 15]

3 **(a)** The graph below shows the trend in boiling points of some of the chlorides of the elements in Period 3 of the Periodic Table. However, there are two boiling points that are wrongly represented.



Account, in terms of structure and bonding of the chlorides, for the error in

(i) region **I**

$MgCl_2$ has a giant ionic structure while $AlCl_3$ has a simple molecular structure. More energy is required to overcome the electrostatic forces of attraction between Mg^{2+} and Cl^- compared to dispersion attraction between $AlCl_3$ molecules. Hence $MgCl_2$ should have a higher boiling point.

(ii) region **II**

Both PCl_3 and SCl_2 have simple molecular structures. More energy is required to overcome the stronger dispersion forces and dipole–dipole attractions between PCl_3 compared to SCl_2. Hence PCl_3 should have a higher boiling point.

[4]

(b) When chlorides of the elements in Period 3 are added to water, some simply dissolve while others are observed to hydrolyse in water.

(i) Write equations to show the behaviour of $AlCl_3$ and PCl_3 in water, clearly indicating whether they refer to dissolution or hydrolysis.

Dissolution: $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$
Hydrolysis: $[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$
Hydrolysis: $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$

(ii) Phosphorus also forms the higher chloride, PCl_5. When PCl_5 is added to water, liquid phosphorus oxychloride, $POCl_3$ is formed as an intermediate compound. Reactions of covalent chlorides with water can be rationalised as step–wise replacement of –Cl with –OH. Deduce a three–step reaction sequence for the formation of $POCl_3$ from PCl_5.

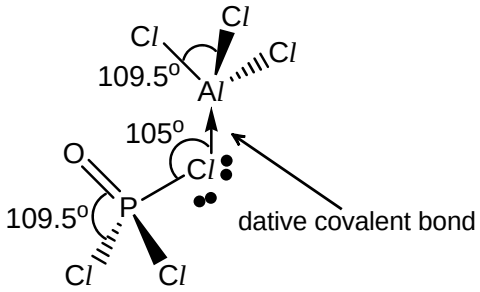
Step 1: $PCl_5 + H_2O \rightarrow PCl_4OH + HCl$
Step 2: $PCl_4OH + H_2O \rightarrow PCl_3(OH)_2 + HCl$
Step 3: $PCl_3(OH)_2 \rightarrow POCl_3 + H_2O$

$POCl_3$ is used in industry as a *Lewis base* to remove the catalytic $AlCl_3$ at the end of a Friedel–Crafts reaction, resulting in the formation of a covalent product.

(iii) Define the term '*Lewis base*'.

A Lewis base is an electron–pair donor.

(iv) Hence draw the full structural formula of the product which results in the removal of $AlCl_3$, stating the type of bonding present.



[8]

(c) There are seven Periods in the Periodic Table at present. However, the recent alleged discovery of an element with atomic number 122 suggests an 'island of stability' beyond the known Periodic Table.
If this claim is true, it will require a new block of the Periodic Table, corresponding to the occupancy of another type of subshell, beyond ***s***, ***p***, ***d*** and ***f***. This is predicted to be a ***g*** subshell, which will be found in the 5th shell of an atom, i.e. the 5***g*** subshell.

(i) Based upon the sequence of subshells in the Periodic Table, ***s***, ***p***, ***d***, ***f***, predict the total number of orbitals in a ***g*** subshell.

9 orbitals

Following Aufbau's Principle, the 17 lowest energy subshells in which electrons are filled are shown below.

1s			
2s	2p		
3s	3p	3d	
4s	4p	4d	4f
5s	5p	5d	
6s	6p		
7s			

(ii) Predict the total number of elements in Period 8 of the Periodic Table.

1s				
2s	2p			
3s	3p	3d		
4s	4p	4d	4f	
5s	5p	5d	**5f**	**5g**
6s	6p	**6d**	**6f**	
7s	**7p**	**7d**		
8s	**8p**			

Period 8 begins with the filling of the 8s subshell and ends with the 8p subshell. Based on Aufbau principle, the subshells in Period 8 will include 8s, 5g, 6f, 7d, 8p.
Total elements = 2 (s) + 6 (p) + 10 (d) + 14 (f) + 18 (g)
= 50

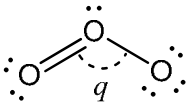
(iii) Element 122 has been given the temporary name 'Unbibium' and has an elemental symbol 'Ubb'. It is predicted to form a chloride of the formula UbbCl_3. Predict the electronic configuration of Ubb in the chloride (after the radon configuration).

Ubb: $[_{86}Rn]\ 5f^{14}\ 5g^2\ 6d^{10}\ 7s^2\ 7p^6\ 8s^2$
Ubb^{3+}: $[_{86}Rn]\ 5f^{14}\ 5g^2\ 6d^{10}\ 7s^2\ 7p^5$

[3]

[Total: 15]

4 **(a)** Ozone, O_3, has the following structure.

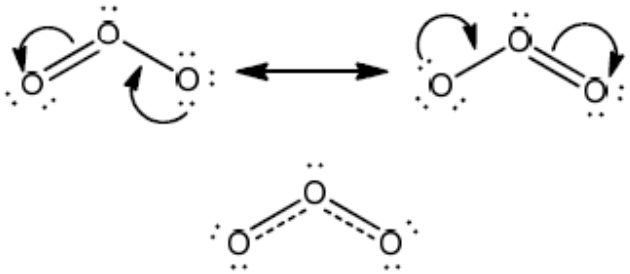


ozone

Bond type	Bond length /Å
O–O	1.48
O=O	1.21

(i) The separation between any two adjacent oxygen atoms in ozone is 1.28 Å. Explain this bond length with suitable chemical structure(s).

Ozone exists as a resonance hybrid.



Show electron movement
Show 1.5 bond in ozone structure

(ii) Suggest a value for angle q.

116 - 118^o (accept any value between)

[3]

(b) Ozone, O_3, is unstable with respect to decomposition to diatomic oxygen:

$$2O_3(g) \rightleftharpoons 3O_2(g) \qquad K_p = 4.0 \times 10^{28} \text{ at r.t.p}$$

(i) Write the K_p expression for the decomposition of ozone to diatomic oxygen.

$$K_p = \frac{(p_{O_2})^3}{(p_{O_3})^2}$$

(ii) Ozone occurs quite readily in nature most often as a result of lightning strikes that occur during thunderstorms.
Calculate the partial pressure of oxygen present in 10^6 m^3 of air at rtp after a lightning strike. Assume that the atmosphere of the Earth is 21 % oxygen by volume.

At r.t.p, atmospheric pressure = 101×10^3 Pa
By Dalton's law of partial pressure,
Partial pressure of O_2 = ($0.21 \times 101 \times 10^3$) Pa = 21 210 Pa

(iii) Hence, calculate the number of O_3 molecules present at equilibrium in 10^6 m^3 of air at rtp after a lightning strike.

$$K_p = \frac{(p_{O_2})^3}{(p_{O_3})^2}$$

$$p_{O_3} = \sqrt{\frac{(p_{O_2})^3}{K_p}}$$

$$= \sqrt{\frac{(21\ 210)^3}{4.0\ ?\ 10^{28}}}$$

$$= ?\ .39\ ?\ 10^{-16}\ \text{Pa (3 sf)}$$

No. of ozone molecules in 10^6 m^3 of air after lightning strike

$$= \frac{\frac{\text{partial pressure of ozone}}{\text{atmospheric pressure}} \text{ 譾olume of air}}{\text{molar volume}} ?\ .02?\ 0^{23}$$

$$= \frac{\frac{2.3854 \times 10^{-16}}{101 \times 10^3} ?\ 0^6}{24 \times 10^{-3}} ?\ .02?\ 0^{23}$$

= 3.82 × 10^{18} molecules

[4]

(c) Ozone can be "good" or "bad" for people's health and for the environment, depending on its location in the atmosphere.
The stratosphere or "good" ozone layer extends upward from about 8 to 50 km and has been gradually depleted by man-made chemicals like chlorofluorocarbons (CFCs).
Once trichlorofluoromethane (CFC-11) is in the stratosphere, there is an initial homolytic fission of a C–C*l* bond in CFC-11 to give C*l* radical. Ozone depletion then proceeds via a four-step mechanism.

Step 1 The initial reaction is between the C*l* radical and ozone to give C*l*O radical and O_2 molecule.
Step 2 Two C*l*O radicals react to give a C*l*OOC*l* molecule.
Step 3 The C*l*OOC*l* molecule dissociates to give C*l*OO and C*l*
Step 4 The C*l*OO radical dissociates to give a C*l* radical and an oxygen molecule

(i) Suggest the energy source for the homolytic fission of the C–C*l* bond in CFC-11.

Ultraviolet (UV) rays from the sun

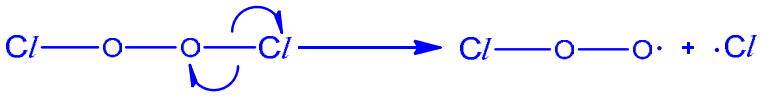
(ii) Use the information given above to outline the full mechanism for the reaction between CFC-11 and ozone. You are advised to draw full structural formulae for all species, so that it is clear which bonds are broken and which are formed.

Indicate any unpaired electrons by a dot (•).

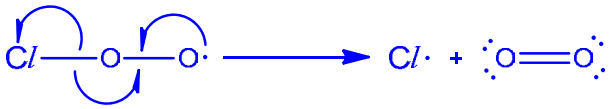
Step 1

Step 2

Step 3



Step 4



(iii) A single C*l* radical would keep on destroying ozone for up to two years.

What is the role of the C*l* radical in the reaction between CFCs and ozone?

C*l* radical acts as a homogenous catalyst because it is not consumed in the reaction.

[6]

(d) Nitric oxide, NO, is another molecule responsible for a small portion of the depletion of ozone. It can be produced in as shown.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

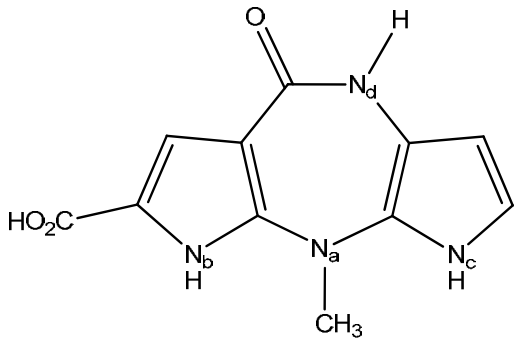
Under standard conditions at 298 K, $K_p = 4 \times 10^{-31}$ but at 2000 K, $K_p = 3 \times 10^{-5}$. Comment on the change in the value of K_p as the temperature rises and explain its importance to the composition of the exhaust gas from cars.

The K_p for the equilibrium reaction increases drastically when the temperature is increased from 298 K to 2000 K.
Exhaust gas from cars contains NO gas because of the reaction between atmospheric nitrogen and oxygen in the hot internal combustion car engine.
Exhaust gas will contain a high proportion of NO gas as forward reaction is favoured due to an endothermic enthalpy change.

[2]

[Total: 15]

5 A derivative of an anti-viral drug, nevirapine (compound **A**), is recently found to be effective in treatment against AIDS and AIDS-related opportunistic infections. Compound **A** has 4 nitrogen atoms labelled N_a to N_d.



compound **A**

(a) Name all the functional groups present in compound **A**.

Secondary amine, tertiary amine, amide, alkene and carboxylic acid

[2]

(b) **(i)** The nitrogen atoms labelled, N_b and N_c, are part of two planar aromatic rings. State the type of hybridisation exhibited by N_b and N_c.

sp^2 hybrid orbital

(ii) The nitrogen labelled, N_a, is the most basic among the 4 nitrogen atoms. Rank the basicity of the other 3 nitrogen atoms from the most basic to the least basic. Explain the order of the basicity of the 3 nitrogen atoms you have ranked.

$N_c > N_b > N_d$

Carboxylic acid is an electron withdrawing inductive group and will decrease the availability of lone of pair of electrons on N_b for donation. Lone pair of electrons on N_d is unavailable for donation due to interaction with the π electrons of the C=O bond.

[3]

(c) Compound **A** exists mainly as zwitterions. Two physical properties of compound **A** are described as follows. Account for the physical properties using equation(s) when appropriate.

(i) Compound **A** has high melting point and exists as a crystalline solid at room temperature and pressure.

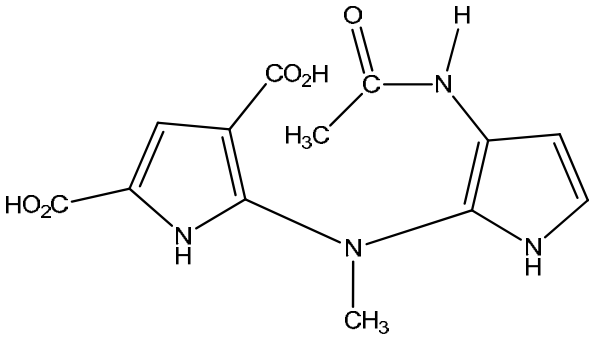
Compound A exists as zwitterions and are held together by strong ionic bonds throughout the giant ionic lattice. A large amount of heat energy is needed to overcome the strong electrostatic forces of attraction between oppositely charged ions.

[1]

(ii) The pH remains relatively constant when a small amount of base is added to a solution of compound **A**.
Positively charged amine salt, being acidic, helps to neutralize added OH^- and maintains pH. A large reservoir of zwitterions ensures sufficient removal of OH^-.

[2]

(d) Compound **A** can be synthesized from compound **B** via a 3-step synthesis route.



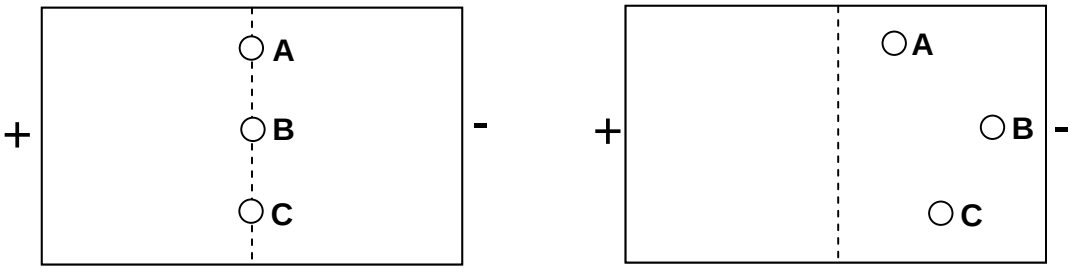
compound **B**

State the reagents and conditions needed for each step.

Step	Reagents and conditions
1	**aq. HC*l*, reflux followed by controlled basification using aq. NaOH, room temperature**
2	**PCl_5, room temperature (or PCl_3 , reflux or SOCl_2, reflux)**
3	**Add water, room temperature**

[3]

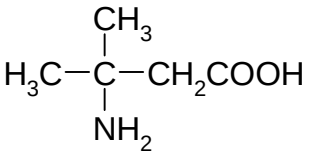
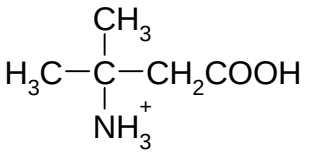
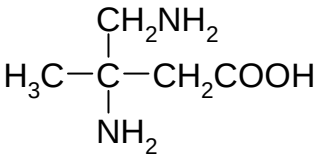
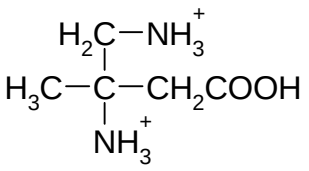
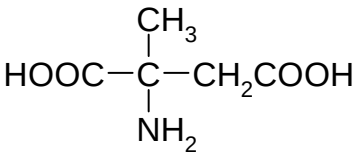
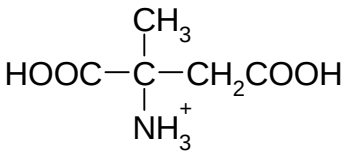
(e) Electrophoresis is a technique used to identify different amino acids. In a particular electrophoresis experiment, a piece of rectangular filter paper is soaked in an aqueous solution of pH 3 and three amino acids are dotted onto the middle of the paper. The positions of the amino acids are labelled **A**, **B** and **C** and a potential difference is then applied. After a while, the paper is sprayed with a colouring chemical to locate the amino acids.



At the start of experiment

At the end of experiment

(i) The structures of the three amino acids being investigated in the experiment are shown below. Draw the corresponding form of the amino acids at pH 3 in the corresponding box.

 **P**	• 
 **Q**	• 
 **R**	• 

(ii) Which of the three amino acids **P, Q or R** in **(i)** corresponds to dot **B** at the end of the experiment? Briefly explain your answer.

Q corresponds to dot B. Q has the highest ionic charge (or ionic charge to size ratio) among the three amino acids. Hence it will be most strongly attracted to the negative plate.

[4]

[Total: 15]