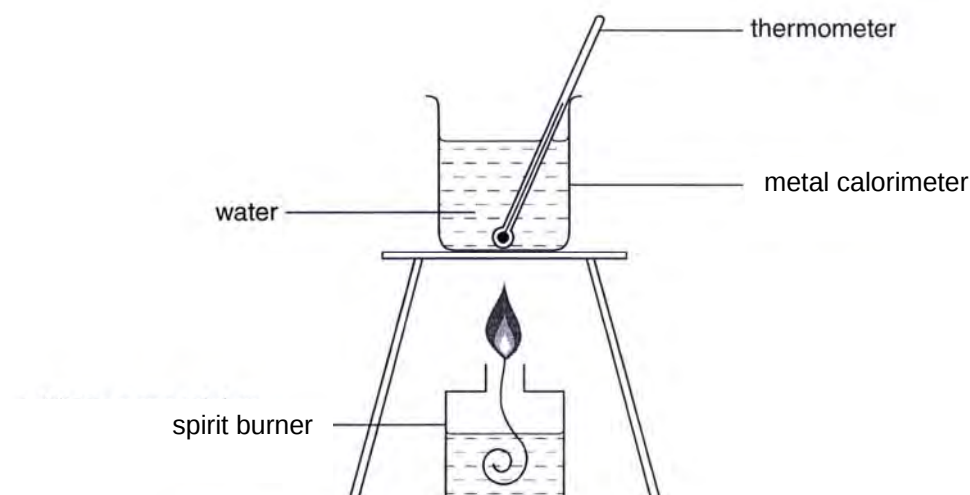


Answer **all** the questions in the space provided.

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 $4.2 \text{ J cm}^{-3} \text{ K}^{-1}$

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

.....
[1]

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

Errors

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Improvements

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[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.

[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.

[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 ($1 \text{ ppm} = 1 \text{ mg dm}^{-3}$). 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.

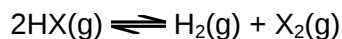
- (i) Calculate the maximum amount of chlorine gas that could have been released from one of the cylinders that was used at Ypres on 22 April 1915.

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

- (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.

[4]

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



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

Temperature /°C	K_c values for dissociation of HX		
	HCl	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.

[3]

- (c) Aqueous solutions of HCl, 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.

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[2]

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

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

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

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

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[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.

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

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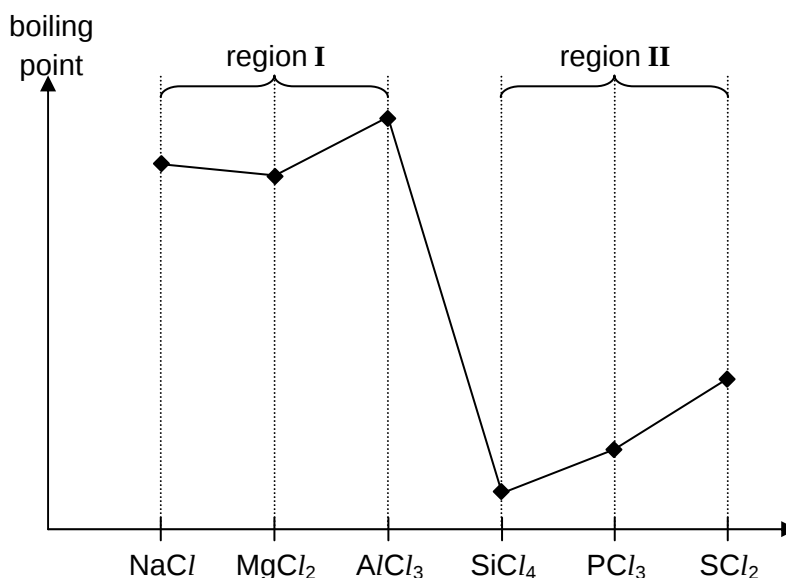
- (iii) Give one domestic use for sodium chlorate(I).

.....

[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

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- (ii) region II

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[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 AlCl₃ and PCl₃ in water, clearly indicating whether they refer to dissolution or hydrolysis.

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- (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 $-\text{Cl}$ with $-\text{OH}$. Deduce a three-step reaction sequence for the formation of POCl_3 from PCl_5 .

Step 1

.....

Step 2

.....

Step 3

.....

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*'.

.....

- (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 **5g** 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.

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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.

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- (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).

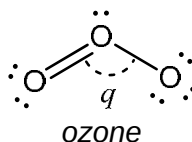
Ubb: $[\text{}_{86}\text{Rn}]$

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[3]

[Total: 15]

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



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).

- (ii) Suggest a value for angle q .

.....°

[3]

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



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

[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–Cl bond in CFC-11 to give $Cl\cdot$ radical. Ozone depletion then proceeds via a four-step mechanism.
- Step 1** The initial reaction is between the $Cl\cdot$ radical and ozone to give $ClO\cdot$ radical and O_2 molecule.
- Step 2** Two $ClO\cdot$ radicals react to give a $ClOOC l$ molecule.
- Step 3** The $ClOOC l$ molecule dissociates to give $ClOO\cdot$ and $Cl\cdot$
- Step 4** The $ClOO\cdot$ radical dissociates to give a $Cl\cdot$ radical and an oxygen molecule

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

.....

- (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

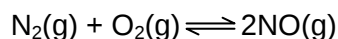
Step 4

- (iii) A single Cl• radical would keep on destroying ozone for up to two years. What is the role of the Cl• radical in the reaction between CFCs and ozone?

.....

[6]

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



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.

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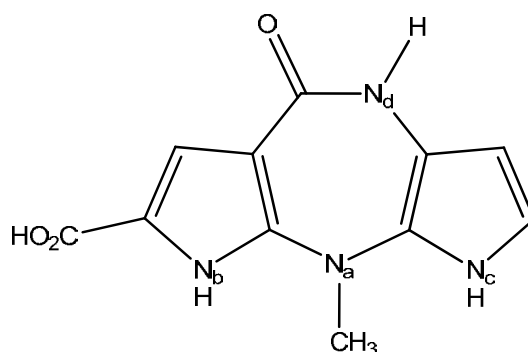
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[2]

[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**.

..... [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 .

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- (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.

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..... [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.

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- (ii) The pH remains relatively constant when a small amount of base is added to a solution of compound **A**.

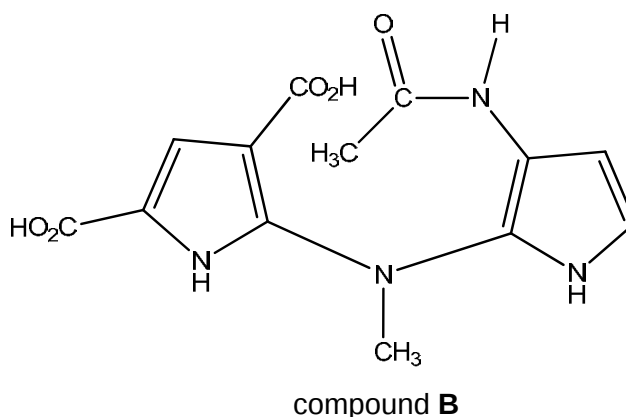
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[3]

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

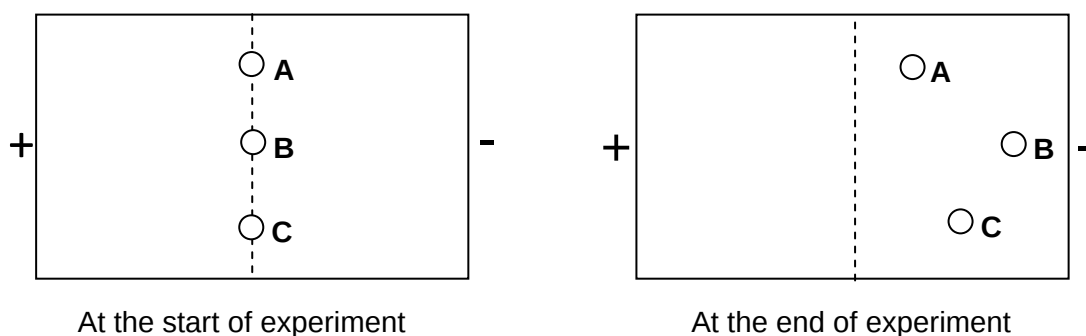


State the reagents and conditions needed for each step.

Step	Reagents and conditions
1	
2	
3	

[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.



- (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.

$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{COOH} \\ \\ \text{NH}_2 \end{array}$ P	
$\begin{array}{c} \text{CH}_2\text{NH}_2 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2\text{COOH} \\ \\ \text{NH}_2 \end{array}$ Q	
$\begin{array}{c} \text{CH}_3 \\ \\ \text{HOOC}-\text{C}-\text{CH}_2\text{COOH} \\ \\ \text{NH}_2 \end{array}$ 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.

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[4]

[Total: 15]