Answer any four questions

- 1 This question involves Period 3 elements and their compounds.
 - (a) Describe the reactions, if any, of the oxides Na₂O and SO₃ with H₂O. Include the approximate pH value of any resulting solutions and write equations for any reaction that occur.

[3]

- (b) An aqueous mixture of NaHCO₃ and Na₂CO₃ can act as a buffer solution.
 - (i) Define the term 'buffer solution'.
 - (ii) With the aid of two equations, explain how a solution of NaHCO₃ and Na₂CO₃ can act as a buffer solution.
 - (iii) Calculate the pH range in which the buffer is most effective, given the following information.

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$
 $K_a = 5.61 \times 10^{-11} \text{ mol dm}^{-3} \text{ at } 25 \text{ }^{\circ}C$

(iv) Calculate the pH change in the solution when the ratio of $[CO_3^{2-}]$ to $[HCO_3^{-}]$ was increased from 0.50 to 0.85.

[7]

(c) When dry chlorine gas is passed over heated aluminium in a hard glass tube, a vapour is produced. The vapour condenses to a yellow-white solid at the cooler part of the tube. At low temperatures, the vapour has the empirical formula $AlCl_3$ and a relative molecular mass of 267.

When a few drops of water are added to the yellow-white solid, steamy white fumes are evolved and a white solid remains. The solid is insoluble in water.

However, when a large amount of water is added to the solid, a weakly acidic solution is formed.

- (i) Suggest the molecular formula of the vapour with empirical $AlCl_3$ and draw a 'dot-and-cross' diagram to describe the bonding.
- (ii) Identify the white solid formed when a small amount of water is added.
- (iii) With an appropriate equation, account for the acidic solution formed. Suggest a pH for this solution.

[5]

(d) When chlorine gas and anhydrous $AlCl_3$ is added to methylbenzene, the following reaction occurs:



- (i) State the type of reaction which occurred.
- (ii) With the aid of equations, outline the mechanism of the above reaction. Use curly arrows to show the movement of electrons.
- (iii) Suggest the structure of the organic product which may form when excess chlorine gas is added to methylbenzene in the presence of sunlight.

[5] [Total: 20 marks] **2** Use of the Data Booklet is relevant in this question.

Sulfuric acid is one of the most important commodity and industrial chemicals, and more of it is produced in the world each year than any other manufactured chemical. It has widely varied uses and is involved in the production of almost all manufactured goods.

(a) Draw the 'dot-and-cross' diagram of H₂SO₄ and suggest the shape and bond angle with respect to S.

[2]

(b) Compound L shown below is able to react with concentrated H₂SO₄ under varied conditions to yield different products. For each of the conditions listed below, draw the structure of the organic product.



Compound L

- (i) Concentrated H₂SO₄, 170 °C
- (ii) CH₃COOH with concentrated H₂SO₄
- (iii) NaBr with concentrated H₂SO₄, heat
- (iv) Concentrated H₂SO₄, followed by H₂O/heat

[4]

(c) The oldest type of rechargeable batteries invented is lead-sulfuric acid batteries, patented by French physicist Gaston Planté in 1859. When the battery discharges, both the positive and negative plates forms lead(II) sulfate, as shown by the equations below:

 $Pb(s) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + 2H^+(aq) + 2e^-$

 $PbO_2(s) + HSO_4(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$

- (i) Using values from the *Data Booklet*, calculate the E°_{cell} of the lead-acid battery during the discharge phase.
- (ii) Write an equation for the overall reaction of the recharge process.

The graphs below measure how the e.m.f. of the lead-sulfuric acid cell and the e.m.f. of another cell **X** change with time.



- (iii) Explain why the e.m.f. of the lead-acid cell decreases over time.
- (iv) Suggest an identity for cell X and explain why the e.m.f. of cell X remains constant.

[4]

- (d) One application of sulfuric acid is in the making of paints. One such paint is chrome yellow, a natural yellow pigment made of lead(II) chromate, which is insoluble in water. The solubility product of PbCrO₄ at 15 °C is 1.69×10^{-14} mol² dm⁻⁶.
 - (i) Write an expression for the solubility product, K_{sp} of lead(II) chromate and hence calculate the solubility of lead(II) chromate in mol dm⁻³.
 - (ii) Concentrated lead(II) nitrate is added dropwise to 0.010 mol dm⁻³ K₂CrO₄, potassium chromate(VI). Assuming the concentration of K₂CrO₄ does not alter with the addition of Pb(NO₃)₂, calculate the maximum concentration of Pb²⁺ ions in the solution before the first trace of precipitation.
 - (iii) In the presence of acid, CrO₄²⁻ forms Cr₂O₇²⁻ readily. In the presence of alkali, CrO₄²⁻ is preferred. Explain this observation.

[5]

- (e) White lead, Pb(OH)₂.PbCO₃ used to be the primary pigment used in paints. However, it has been replaced largely by BaSO₄ and TiO₂, due to the toxicity of lead-based paint. When white lead is heated to decomposition, steam and a colourless gas are evolved. The colourless gas forms a white precipitate when it is passed through limewater.
 - (i) Write an equation for the decomposition of white lead.
 - (ii) Using your answer in (e)(i), calculate the percentage loss in mass upon heating a sample of white lead until no further change occurs.
 - (iii) Assuming Ca(II) compounds decomposes to form similar compounds as Pb(II) compounds, explain whether you would expect the temperature required for the decomposition of Ca(OH)₂.CaCO₃ to be higher or lower than that of white lead.

[5] [Total: 20 marks]

- **3** By observing the kinetics of organic reactions, scientists are able to deduce their mechanisms.
 - (a) In an experiment, the hydrolysis of 2-bromo-2-methylpropane, (CH₃)₃CBr with aqueous sodium hydroxide is found to be first order with respect to (CH₃)₃CBr and zero order with respect to OH⁻. The half-life of the reaction is found to be 5 minutes.
 - (i) Calculate the value of the rate constant, giving its unit.
 - (ii) The initial concentration of (CH₃)₃CBr is 1.6 mol dm⁻³. Sketch a graph of concentration of [(CH₃)₃CBr] against time, clearly indicating the time taken for 2-bromo-2-methylpropane to decrease to 6.25 % of its original concentration.

[3]

(b) In another experiment, the hydrolysis of 2-bromopropane, (CH₃)₂CH(Br) is being investigated. Samples of 2-bromopropane are dissolved in dilute aqueous ethanol (80% ethanol and 20% water by volume) and reacted with sodium hydroxide solution under heat. The rate equation is found to be as follows:

Rate = $(0.24 \times 10^{-5}) [(CH_3)_2CH(Br)] + (4.7 \times 10^{-5}) [(CH_3)_2CH(Br)][OH^-]$

- (i) The rate equation obtained shows the hydrolysis of 2-bromopropane exhibiting a mixture of first and second order kinetics, following mechanisms of S_N1 and S_N2 respectively. Suggest why this may be so.
- (ii) Describe the reaction mechanism of the S_N2 part of the reaction of 2-bromopropane with OH⁻ ions. Use curly arrows to indicate the movement of electrons.
- (iii) The percentage at which the respective mechanisms contribute to the overall rate is known as the percentage rate.

For the second order kinetics in this reaction, the percentage rate given is as follows:

% rate =
$$\frac{4.7[OH]}{4.7[OH^-] + 0.24} \times 100$$

Using the above information, calculate the percentage rate for the $S_N 2$ mechanism in this reaction for the following concentrations of OH⁻ ions.

- (1) 0.01 mol dm⁻³
- (2) 0.1 mol dm⁻³
- (3) 1.0 mol dm⁻³
- (iv) Using your answer in (b)(iii), state and explain how the percentage rate for S_N2 is dependent on the concentration of OH⁻.
- (v) From the rate equation, the S_N2 kinetics is characterised by a larger rate constant than the S_N1 kinetics. Hence or otherwise, construct a Maxwell-Boltzmann distribution curve for the hydrolysis of 2-bromopropane. In the curve, indicate clearly the activation energies for the 2 different pathways as E_{a1} for the S_N1 pathway and E_{a2} for the S_N2 pathway.
- (vi) Suggest the reagents and conditions used in the conversion of (CH₃)₂CH(Br) to (CH₃)₂CHCOOH.

[10]

6

- (c) Halogenoalkanes are widely used as commercial products such as fire extinguishers and refrigerants. However, varied halogenoalkanes such as C₂H₅C*l*, C₂H₅Br and C₂H₅I differ in their physical and chemical properties.
 - (i) Suggest and explain how the boiling points of C_2H_5Cl , C_2H_5Br and C_2H_5I differ.
 - (ii) Describe and explain how C₂H₅C*l*, C₂H₅Br and C₂H₅I would differ in reactivity towards aqueous sodium hydroxide.

[4]

(d) Another halogen containing compound is titanium bromide. To determine the formula for a titanium bromide sample, $TiBr_x$, electrolysis was conducted on molten titanium bromide using the apparatus shown below.



molten titanium bromide

The results of the experiment were as follow:

Ammeter reading –0.5 ADuration of current flow –1 hour and 30 minutesMass of titanium produced –0.45 g

- (i) Identify the electrode (I or II) at which the titanium was produced.
- (ii) Determine the value of x in TiBr_x.

[3]

[Total: 20 marks]

- 4 Phenol has antiseptic properties and is a powerful disinfectant. Hence, it is found in medicinal products such as ear and nose drops, throat lozenges and mouthwashes.
 - (a) The standard enthalpy change of combustion of phenol is -3054 kJ mol⁻¹.
 - (i) Using the data given above with the following standard enthalpy changes of formation, construct a suitable energy cycle diagram to calculate the standard enthalpy change of formation of phenol.

 $\Delta H_{f}^{\circ}(\mathrm{CO}_{2}) = -394 \text{ kJ mol}^{-1}$ $\Delta H_{f}^{\circ}(\mathrm{H}_{2}\mathrm{O}) = -286 \text{ kJ mol}^{-1}$

(ii) Given the standard entropy change for the formation of phenol is $-384 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$, calculate the standard Gibbs Free Energy, ΔG° , for the formation of phenol.

[3]

(b) 2,4,6-trichlorophenol, a chlorinated phenol, is a stronger germicide than phenol.



2,4,6-trichlorophenol

- (i) Predict and explain whether 2,4,6-trichlorophenol has a larger or smaller K_a value compared to phenol.
- (ii) Describe a suitable chemical test to distinguish between 2,4,6-trichlorophenol and phenol.

[3]

(c) 1-napthol is a derivative of phenol. The following reaction scheme involves synthesising compound **Q** from 1-napthol.



- (i) Suggest a suitable structure for **P**.
- (ii) Suggest the reagents and conditions for Step II.
- (iii) Explain why 1-napthol is more soluble in water than compound **Q**.

[4]

- (d) An alkaline solution of compound Q from (c) can act as a bidentate ligand when added to a blue solution of aqueous CuSO₄. A pale blue precipitate R is formed. Analysis of R shows that its formula is Cu(C₁₀H₈NO)₂(H₂O)₂.
 - (i) Draw the structural formula of **R**, showing the arrangement of the ligands in the structure.
 - (ii) When concentrated NH₃ is added to **R**, the precipitate dissolves to form a deep blue solution. Identify the substance giving rise to the deep blue solution.

[3]

[Question continues next page.]

(e) Keratin is a fibrous protein and is the key structural material making up the outer layer of human skin. One of the major interactions between the tertiary structures is disulfide bonds. An overdose of copper(II) ions in the body is known to cause disruption of the structure in keratin. At the same time, copper(II) ions are also found to be useful in determining the presence of peptide bonds, when used in an aqueous solution of potassium hydroxide and potassium sodium tartarate. This test is known as the Biuret test.

The initial Biuret reagent is blue in colour. The aqueous tartarate ions bind to Cu²⁺ as ligands, giving the bistartrato cuprate(II) as shown.



- (i) Explain why the initial Biuret reagent is coloured.
- (ii) In the presence of proteins, the Biuret reagent reacts with peptide bonds in the proteins to form a complex as shown.



The solution turns from blue to violet. Suggest what caused the colour change in the Biuret reagent.

- (iii) Explain in chemical terms which R-group interactions in keratin were disrupted in the presence of Cu²⁺ ions.
- (iv) Describe how proteins and polypeptides can be broken down into amino acids in the laboratory without the use of enzymes.

[7]

[Total: 20 marks]

- **5** Iron is the fourth most abundant element on Earth, accounting for 4.71% of the elemental mass in the planet's crust. In the human body, iron is the twelfth most abundant element, constituting 0.004% of the body mass.
 - (a) Consider the following equilibrium at a constant pressure of *p* atm, using iron as catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
 $\Delta H = -98 \text{ kJ mol}^{-1}$

A mixture of 2.0 moles of nitrogen, 6.0 moles of hydrogen and 4.0 moles of ammonia was placed in a closed vessel at a temperature of 450 K.

When the system has reached equilibrium, it was found that there was only half the original amount of ammonia remaining in the vessel.

- (i) Given the pressure equilibrium constant, $K_p = 5.33$ atm⁻², calculate the value of pressure *p*.
- (ii) Ammonia is produced at high quantities in industries. The figure below shows how the percentage of ammonia in the vessel varies with pressure at temperatures 400 °C and 600 °C respectively.



Sketch graphs to show how the percentage of ammonia in the equilibrium mixture would vary with temperature at pressures 200 atm and 300 atm respectively. Both graphs should be drawn on the same axes.

(iii) Explain why iron is used as a catalyst even though the production of ammonia is an energetically favourable exothermic process.

[6]

(b) In the body, iron is most commonly found in red blood cells, as part of the oxygen-carrying protein haemoglobin. Oxygen molecules are bound to the Fe²⁺ ions of the haem groups, forming oxyhaemoglobin. This binding is affected by molecules such as carbon monoxide, as a result of breathing in tobacco smoke or car exhaust fumes. As a result, when exposed to concentrated amounts of carbon monoxide gas for prolonged periods, victims would suffer from insufficient oxygen diffusion, leading up to potentially fatal carbon monoxide poisoning.

Vanabins are vanadium-associated proteins hypothesised to carry oxygen in the blood, functioning like haemoglobin. Vanabins are commonly found in sea organisms like sea squirts.

- (i) Explain how carbon monoxide binds to the Fe^{2+} centre of the haem group.
- (ii) Explain why vanadium can bind with oxygen, like iron.

(iii) The concentration of vanadium found in the blood of sea squirts is around 100 mM and each sea squirt has around 300 cm³ of blood. Given that one litre of seawater contains 7.1 µg of vanadium and assuming that the sea squirt is 100% efficient in absorbing vanadium from seawater, calculate how many kilograms of seawater each sea squirt has to process to achieve 100 mM of vanadium in their blood.

$$[1 \ \mu g = 1 \times 10^{-6} \text{ g}, 1 \text{ mM} = 1 \times 10^{-3} \text{ mol dm}^{-3}, \text{ density of seawater} = 1.03 \text{ kg} / \text{ litre}]$$

[4]

(c) When aqueous bromine is added to an organic 6-membered cyclic dyestuff S, C₁₀H₁₄O, bromine is decolourised and compound T, C₁₀H₁₄OBr₄ is formed. S is insoluble in aqueous NaOH. Both S and T give silver mirror when reacted with Tollen's reagent. When S is reacted with hot acidified KMnO₄, two organic compounds, U, C₃H₄O₃ and V, C₇H₁₀O₅ are formed. U gives a yellow precipitate when warmed with alkaline aqueous iodine. Effervescence is observed when U is reacted with sodium carbonate. Treatment of V with LiA/H₄ produces a compound with the structure shown below.



Deduce structures **S** – **V** and explain the reactions.

[6]

(d) For the following pairs of compounds, describe a simple chemical test to distinguish the first compound from the second compound. That is, the test should result in a positive test for the first compound.

For each test, state the reagents and conditions and the expected observations.



[4] [Total: 20 marks]

END OF PAPER