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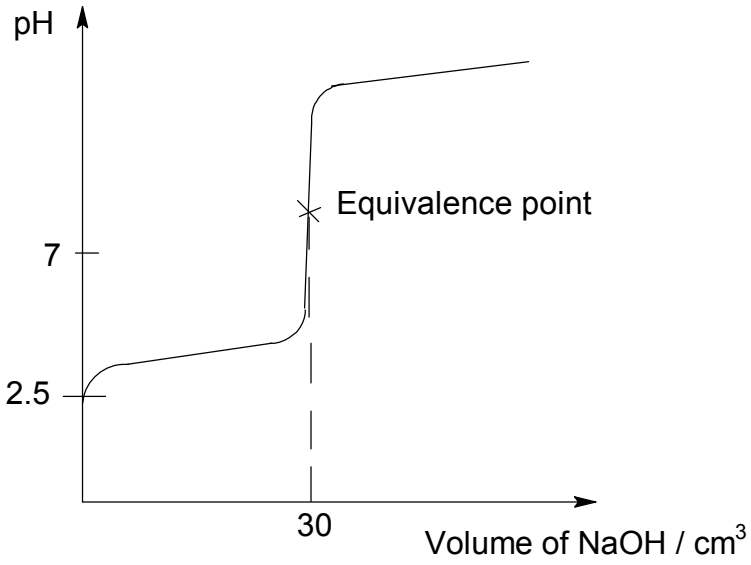
Answer any **four** questions.

1(a) Pyruvic acid, $CH_3COCOOH$, occurs naturally in the body and is an end product of the metabolism of sugar. When 10.0 cm^3 of a solution of pyruvic acid is titrated against 0.01 mol dm^{-3} sodium hydroxide, with a data logger, the following curve is obtained.



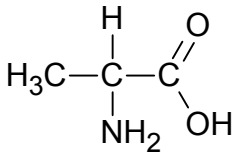
(i) Suggest a suitable indicator, if the titration is to be repeated without the use of a data logger. Explain your reasoning.

(ii) Calculate the value of K_a for pyruvic acid.

(iii) Explain, with the aid of an appropriate equation, why the pH at equivalence point is greater than 7.

[7]

(b) Pyruvic acid is converted to the amino acid, alanine, in just one single step in the body by the enzyme alanine transaminase. However, to achieve the same conversion in a laboratory, multiple steps are required. Given the chemical structure of alanine below, show how pyruvic acid can be converted to alanine in not more than 4 steps. Indicate the reagents, conditions and all intermediates in your answer. The alanine formed from your suggested synthesis steps may be in its cationic, anionic or zwitterionic forms.



Alanine

[5]

[Turn Over

(c) Alanine, together with the 19 other standard amino acids are the building blocks of proteins. State the two factors that cause protein denaturation and explain how the two stated factors denature the protein. [4]

(d) When 0.200 g of alanine is subjected to complete combustion, carbon dioxide, nitrogen dioxide and water is formed. The gases produced are absorbed by 20 cm^3 of 1.5 mol dm^{-3} aqueous sodium hydroxide. The resultant solution is then titrated with 0.3 mol dm^{-3} H_2SO_4. Calculate the volume of H_2SO_4 required for the mixture to reach equivalence point. [4]

Hint: $2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O$

[Total: 20]

2(a) Hydrogen chloride gas and ammonia gas react to form ammonium chloride.

$$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$$

(i) By constructing a Hess' Law Cycle, calculate the standard enthalpy change of the reaction, given the following information:

$$\Delta H^{\theta}_{f(NH_3)} = -46.1 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{f(HCl)} = -92.3 \text{ kJ mol}^{-1}$$
$$\Delta H^{\theta}_{f(NH_4Cl)} = -314.4 \text{ kJ mol}^{-1}$$

(ii) The standard entropy change of the reaction is –284 J K^{-1} mol^{-1}. Explain why this value is negative.

(iii) State and explain whether the reaction is spontaneous at high or low temperatures.

(iv) Calculate the temperature for which the reaction is spontaneous.

[6]

(b) When hydrogen chloride gas is added to organic compound **P**, C_6H_{12}, two products **Q** and **R**, which are isomers of each other, $C_6H_{13}Cl$, are formed in unequal proportion. When **Q** and **R** are separately boiled with aqueous sodium hydroxide, **S** is formed from **Q**, while **T** is formed from **R**. **S** and **T** are also isomers of each other, with the same molecular formula, $C_6H_{14}O$. When **S** and **T** are separately boiled with acidified potassium manganate(VII), no decolourisation is observed in the test tube containing **S**; while decolourisation is observed in the test tube containing **T** which results in the formation of **U**, $C_6H_{12}O_2$. When some sodium carbonate powder is added to **U**, effervescence of carbon dioxide gas is observed. When **P** is boiled with acidified potassium manganate (VII), compound **V**, $C_5H_{10}O$ and CO_2 are formed. **V** gives an orange precipitate when warmed with 2,4-dinitrophenylhydrazine. When **V** is heated with lithium aluminium hydride in dry ether, **W**, $C_5H_{12}O$, which does **not** exhibit optical activity, is formed.

Deduce the structures for each lettered compound, **P** to **W**. Explain the chemistry of the reactions involved. Balanced equations are not required. [12]

(c) Using relevant information from the *Data Booklet*, compare and explain the relative acid strength of HCl and HF. [2]

[Total: 20]

3 $AlCl_3$ is a compound of aluminium and chlorine. The solid has a low melting and boiling point and it is covalently bonded. It finds widespread application in the chemical industry as the classic catalyst for the Friedel-Crafts alkylation reaction. Typically, $AlCl_3$ can be used to catalyse the reaction between benzene and chloromethane.

(a) Describe the mechanism for the reaction between benzene and chloromethane. [3]

(b) $C_6H_5CH_2Cl$ can be obtained by reacting $C_6H_5CH_3$ with Cl_2 via a free radical substitution.

(i) By making use of relevant bond energies from the *Data Booklet*, calculate the enthalpy change of this reaction.

(ii) Give two reasons why the actual enthalpy change of this reaction deviates from the above value.

[4]

(c) Another metal chloride **A**, which has the formula MCl_x cannot be used to catalyse the reaction between benzene and chloromethane.

When 1.0×10^{-3} moles of aqueous sodium hydroxide is reacted completely with 5.0×10^{-4} moles of **A**, 0.0292 g of a white precipitate, **B** is formed. When **B** is heated, water is lost leaving a white residue **C**. **C** is of high melting point and it is very slightly soluble in cold water.

(i) Deduce the identities of **A**, **B** and **C**. Write equations wherever applicable.

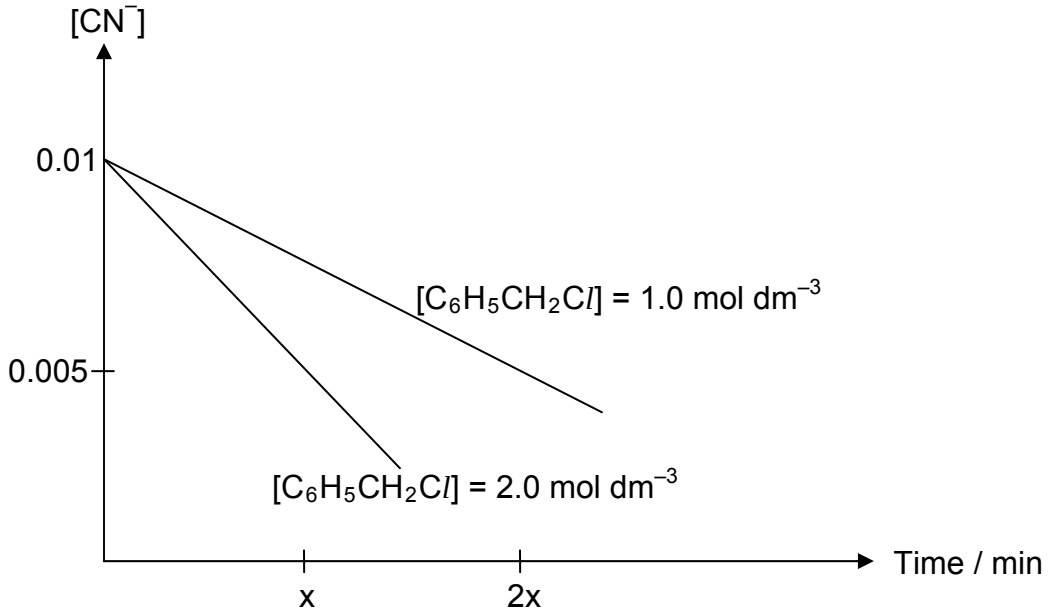
(ii) Predict the pH of the solution formed when **A** is dissolved in water.

[6]

(d) The reaction below is an example of nucleophilic substitution.

$$C_6H_5CH_2Cl + CN^- \rightarrow C_6H_5CH_2CN + Cl^-$$

The reaction kinetics of this reaction is determined by monitoring the change in the concentration of CN^- with time. The results are shown below:



(i) Determine the rate equation for the above reaction.

(ii) With the aid of Maxwell-Boltzmann distribution curve, predict and explain the effect on the rate of this reaction when the reaction temperature is decreased.

[7]

[Total: 20]

4 The oldest church in Paris named Saint-Germain I'Auxerrois, is well-known for its splendid stained glass. The components of the stained glass used in the church windows is known to contain lead(II) oxide, silicon(IV) oxide and traces of a chromium-containing oxide.

(a) Explain why transition metals are denser than s-block elements. [3]

(b) Describe the bonding in the following substances and explain why it contributes to the specified property in glass:

substance	property
(i) silicon (IV) oxide	hardness
(ii) lead (II) oxide	Electrical conductivity (if any)

[4]

(c) The window frames enclosing the stained glass is made of aluminium due to its low density and high melting point.

Account for the high melting point of aluminium. [2]

(d) Construct a Born-Haber cycle for the formation of lead(II) oxide from its elements. Use the relevant data from the table below as well as from the *Data Booklet*, calculate the lattice energy of lead(II) oxide.

enthalpy term	ΔH / kJ mol^{-1}
standard enthalpy change of formation of PbO	–219
standard enthalpy change of atomisation of Pb	+196
first electron affinity of oxygen	–141
second electron affinity of oxygen	+790

[6]

(e) It is found that a famous painting brought to an art gallery for cleaning and restoration before being hung in the St Germain church, has darkened because of the formation of lead(II) sulfide, PbS. Gentle treatment of the darkened areas of the painting with a dilute solution of hydrogen peroxide restores the original bright colours. The hydrogen peroxide converts the black lead(II) sulfide to white lead(II) sulfate. $E^{\theta}_{PbSO_4/PbS}$ in acidic medium has a value of + 0.45 V.

(i) With the aid of the *Data Booklet* or otherwise, construct an overall equation for the reaction of hydrogen peroxide with lead(II) sulfide and calculate the overall electrode potential for the reaction.

(ii) State the role of hydrogen peroxide in this reaction.

[5]

[Total: 20]

5 This question is about compounds commonly used as chlorinating agents in organic synthesis such as PCl_3, PCl_5 and $SOCl_2$.

(a) Draw the Lewis structures of PCl_5 and $SOCl_2$, state their shapes. [4]

(b) Predict the solubility of PCl_5 in CCl_4. Support your prediction with appropriate reasons. [3]

(c) PCl_5 can be produced by reacting PCl_3 with chlorine gas. When a mixture containing 1:1 ratio of PCl_3 and Cl_2 at a total initial pressure of 3.8 atm is allowed to react at 700 K, the partial pressure of PCl_5 formed at equilibrium is found to be 1.68 atm. The standard enthalpy change of this reaction is –418 kJ mol^{-1}.

(i) Calculate the equilibrium partial pressures of PCl_3 and Cl_2.

(ii) Hence, determine the percentage conversion of PCl_3 and the equilibrium constant, K_p.

(iii) Using Le Chatelier's Principle, predict the effect on the yield of PCl_5 when the temperature is increased.

[7]

(d) Adipic acid, $HOOC(CH_2)_4COOH$ which is the most important dicarboxylic acid used in the industrial production of nylon, can be converted into its acid chloride by treatment with thionyl chloride, $SOCl_2$. In the production of nylon-66 which is a polymer, adipic acid is heated with hexamethylenediamine, $H_2N(CH_2)_6NH_2$ at 280°C.

(i) A solution of adipic acid has a pH value of 4.4. Suggest a possible pH value of its acid chloride, giving your reason.

(ii) Suggest a suitable chemical test to distinguish between adipic acid and hexamethylenediamine.

[6]

[Total: 20]

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