2009 H2 Chemistry 9746/2 Suggested Answers

1

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

1 Hydrogen cyanide was first isolated from a blue dye (Prussian blue) which had been known since 1704 and is now known to be a coordination polymer, Fe^{III}₄[Fe^{II}(CN)₆]₃.

In the year 2000, 732,552 tonnes of HCN were produced in the US. The most important process for HCN production is the Andrussov oxidation in which methane and ammonia react in the presence of oxygen at about 1200 °C:

 $2CH_4 + 2NH_3 + 3O_2 \rightarrow 2HCN + 6H_2O$

The energy needed for the reaction is provided by the partial oxidation of methane and ammonia. (1 tonne = $1\ 000\ \text{kg}$)

HCN is also obtainable from fruits that have a pit, such as cherries, apricots, apples, and bitter almonds. Many of these pits contain small amounts of cyanohydrins such as mandelonitrile and amygdalin, which slowly release hydrogen cyanide. An article mentioned that 100 g of crushed apple seeds can yield about 10 mg of HCN.

(a) (i) Draw the structure of the anion of Prussian blue to show its shape. Indicate on the structure the bond angle and give the name of the shape.

Structure:



Bond angle must be ON the structure. Correct structure drawn (pls draw dotted lines to show square plane).

Shape: Octahedral

(ii) Using specific examples from the information above, state two characteristic properties of transition elements.

They are able to show variable oxidation states. (e.g. $Fe^{III}_{4}[Fe^{II}(CN)_{6}]_{3}$, Fe^{III} is +3 O.S. but Fe^{II} is +2 O.S.) They are able to form <u>stable complex compounds or ions</u>. (e.g. $Fe^{II}(CN)_{6}]_{3}^{4-}$ complex ion)

2

They are able to form <u>coloured compounds and ions</u>. (e.g. Prussian blue)

[Only two properties required. For each property, specific example must be given.]

(iii) Find the percentage by mass of cyanide in Prussian blue.

Percentage by mass of cyanide in Prussian blue

$$= \frac{26.0 \times 6 \times 3}{3[(26.0 \times 6) + 55.8] + (4 \times 55.8)} \times 100\%$$
$$= \frac{468.0}{858.6} \times 100\%$$
$$= 54.5\%$$

[5]

(b) (i) Assuming that the amount of HCN produced in the US annually is the same, calculate the number of moles of HCN produced in the US from 2000-2002.

Total mass of HCN produced in 3 years $= 732,552 \times 3$ = 2.20 x 10⁶ tonnes

Mr of HCN = 1.0 + 12.0 + 14.0 = 27.0 No. of moles of HCN = $\frac{2.20 \times 10^6 \times 10^6}{27.0} = \frac{8.15 \times 10^{10} \text{ mol}}{27.0}$

(ii) What is volume in dm³ of oxygen gas required via the Andrussov oxidation to form the amount of HCN mentioned in (i) at r.t.p.?

3 $O_2 \equiv 2$ HCN No. of moles of $O_2 = 3/2 \times 8.15 \times 10^{10} = 1.22 \times 10^{11}$ mol Volume of O_2 at r.t.p. = 24 x 1.22 x $10^{11} = 2.93 \times 10^{12}$ dm³

[2]

(c) An apple has an average of 4 seeds and each seed weighs an average of 0.20 g. Find out the mass of HCN that can be yielded from seeds from 10 apples.

Mass of seeds from 10 apples = 10 x 4 x 0.20 = 8.00 g Mass of HCN that can be produced from 10 apples = $\frac{8.00}{100}$ x 10 = 0.800 mg

> [1] **[Turn over**

(d) (i) HCN gas is a highly poisonous gas that can cause permanent damage to the central nervous system. The toxic level of HCN gas in the air is about 0.001 mg dm⁻³.

3

Express the toxic level of HCN gas in the air in terms of mol dm⁻³.

Toxic level of HCN = $\frac{0.001 \times 10^{-3}}{27.0}$ = <u>3.70 x 10^{-8} mol dm^{-3}</u>

(ii) How many molecules of HCN are present at this toxic level in 2 dm³?
 No. of molecules of HCN at this toxic level

 $= \frac{0.001 \times 10^{-3}}{27.0} \times 6.02 \times 10^{23} \times 2$ $= \frac{4.46 \times 10^{16} \text{ molecules}}{10^{16} \text{ molecules}}$

(iii) When it rains, HCN dissolves in water to give an acid solution. If 2 dm³ of air containing the toxic level of HCN dissolves in 20 dm³ of rainwater, find the concentration of HCN in the acid solution.

No. of moles of HCN in 2 dm³ of air = $3.70 \times 10^{-8} \times 2$ = 7.40×10^{-8} mol [HCN] = $\frac{7.40 \times 10^{-8}}{20 \times 10^{3}} \times 10^{3} = 3.70 \times 10^{-9}$ mol dm⁻³ [3]

(e) Name and describe the mechanism for the formation of cyanohydrins starting from propanal and HCN. State any additional reagent that is needed.

Name: Nucleophilic addition

Additional reagent: <u>NaCN (catalyst) or NaOH (trace amount)</u> CN⁻ functions as a <u>nucleophile</u> and it attacks the <u>electron deficient</u> carbonyl carbon. Both curly arrows and partial charges on r.d.s. (slow step) must be shown.



The <u>tetrahedral intermediate</u> is a <u>strong base</u> and quickly captures a proton from HCN.



<u>CN⁼ catalyst is regenerated</u> which then attacks another carbonyl molecule.

[Total: 14] [Turn over

- 2 This question is about Group VII hydrides, HX.
 - (a) The Group VII hydrides show clear trends in the H-X bond energy where X = CI, Br and I. They behave as weak acids in liquid ethanoic acid, dissociating to different extents.
 - (i) Write an equation to show how HX dissociates in ethanoic acid.

 $HX + CH_3CO_2H \Rightarrow CH_3CO_2H_2^+ + X^-$

(ii) Rank the pK_a of the three Group VII hydrides in ethanoic acid in decreasing order. Explain your answer with reference to the *Data Booklet*.

pK_a of acids: HC*l* > HBr > HI From the Data Booklet,

Bond	Bond energy / kJ mol ⁻¹
H—C <i>l</i>	431
H—Br	366
H—I	299

Since the <u>strength of H-X bond decreases</u> down the group due to the <u>increasing atomic radii</u> of the halogen atom (or poorer orbital overlap between the halogen and hydrogen atoms), it becomes <u>easier to dissociate</u> HX down the group.

[2]

(iii) Suggest why the Group VII hydrides are weak acids in ethanoic acid whereas they are strong acids in water.

Ethanoic acid is a <u>weaker base/stronger acid</u> than water. Hence, ethanoic acid is <u>less likely to accept a proton</u> from HX.

Or Since ethanoic acid is a stronger acid than water, it will <u>partially</u> <u>dissociate into H[±] ion</u> in aqueous state, hence, causing the <u>position of</u> <u>equilibrium of HX \Rightarrow H[±] + X⁻ to shift left by common ion effect/ suppress the</u> <u>dissociation of HX by common ion effect</u>. Group VII hydrides are weak acids in ethanoic acid.

[4]

- (b) Another Group VII hydride, HF, behaves as a weak acid. A solution is prepared by dissolving HF in a fixed volume of water. The addition of some barium hydroxide to the solution neutralizes one third of the HF present. The pH of the resulting solution is 2.88.
 - (i) Calculate the concentration of hydrogen ions in the solution after barium hydroxide is added.

$$[H^{+}] = 10^{-2.88} = 1.32 \text{ x } 10^{-3} \text{ mol dm}^{-3}$$

- (ii) Using your answer to (i) and the given information, calculate the value of the acid dissociation constant, K_a, of HF.
 - $K_a = [H^+][F^-] / [HF]$ = 1.32 x 10⁻³ x (1/2) = 6.60 x 10⁻⁴ mol dm⁻³

[3]

(c) The figure below shows two cells connected in series. Cell 1 and Cell 2 involve the electrolysis of saturated solution of CuBr₂ and concentrated HX respectively, where X is one of the Group VII elements.



(i) Using E^{θ} values, write ion-electron equations, for the reactions occurring at the cathode and anode in **Cell 1** during electrolysis. Include state symbols.

Cathode: $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$

Anode: $2Br(aq) \rightarrow Br_2(l \text{ or } aq) + 2e$

After a current was passed through the saturated solution of $CuBr_2$ in **Cell 1** for 10 minutes, the solution surrounding the anode was removed and it was found to require 35.50 cm³ of 0.500 mol dm⁻³ of sodium thiosulphate solution for complete reaction.

(ii) Determine the number of moles of $Na_2S_2O_3$ used.

(iii) Calculate the number of moles of electrons transferred.

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For 5H_2O + S_2O_3^{2^-} \rightarrow 2SO_4^{2^-} + 10H^+ + 8e
Hence, no. of moles of electrons transferred
= 8 x no. of moles S_2O_3^{2^-}
= 8 x 0.0178
= 0.142
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(iv) Hence, determine the current that flows through the circuit.

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Quantity of charge transferred = I \times t
0.142 x 96500 = I \times 10 \times 60
I = 22.8 \text{ A}
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[5]

(d) A halogen is evolved at one of the electrodes in Cell 2 after passing the current through it for 10 minutes and It is found that the mass of the syringe increased by 5.04 g. Identify X by calculating the M_r of the halogen produced.

Since two half cells are connected in series, the current passed through the Cell 2 is also 22.8 A.

No. of moles of electrons transferred = 0.142

From $2X^{-} \rightarrow X_{2} + 2e$, Hence, no. of moles of the gas produced in Cell 2 = $\frac{1}{2} \times 0.142$ = 5.04/ M_r M_r of the gas, X₂= 71.0 Hence, X is C*l*.

[2] [Total: 14]

3 In nature, chlorine is abundantly found as the chloride ion, a component of the salt that is deposited in the earth or dissolved in the oceans.

The melting points of the chlorides of the elements sodium to phosphorus of the third period of the Periodic Table are given below.

compound	sodium chloride	magnesium chloride	aluminium chloride	silicon tetrachloride	phosphorus pentachloride
melting point / °C	808	714	178	-70	162
pH of solution	7	6.5	3	2	2

*sublimes at 178 °C

(a) (i) Account for the difference in the melting points of sodium chloride and silicon tetrachloride, in terms of structure and bonding.

NaC/ is an ionic compound with <u>giant ionic structure</u> held by <u>strong</u> <u>electrostatic forces of attraction between the oppositely charged Na[±] and</u> CF ions.

Silicon tetrachloride has a **simple molecular structure**.

The molecules are non-polar and held by <u>weak induced dipole-induced dipole</u> <u>attractions</u> which can be easily broken during melting.

Since **ionic bonds are much stronger than id-id**, NaC/ melts at a **much higher temperature**.

(ii) Explain briefly the difference in the pH values when MgCl₂, AlCl₃ and PCl₅ are separately dissolved in water. Write equations to support your answer.

Due to <u>high charge density of Mg²⁺</u>, it hydrolyses with water to form a slightly acidic solution.

 $MgCI_2 + H_2O \rightleftharpoons MgCI(OH) + HCI$

Since Al^{3+} has a higher charge density than Mg²⁺ due to its <u>higher charge</u> and smaller ionic radius, it hydrolyses in water to a greater extent, thus the solution formed is more acidic at pH 3.

 $A/CI_3 + 6H_2O \rightarrow [A/(H_2O)_6]^{3+} + 3C/$ $[A/(H_2O)_6]^{3+} \rightleftharpoons [A/(H_2O)_5(OH)]^{2+} + H^+$

When PCI₅ dissolved in water, it forms strong acid of HCI and H₃PO₄. PCI₅ + 4 H₂O \rightarrow H₃PO₄ + 5 HCI

[6]

(b) The reaction of silicon tetrachloride with water produces large amount of heat.

When 3 cm³ of silicon tetrachloride is added to 100 cm³ of water at 5.0 $^{\circ}$ C, the temperature of the water rises to 9.2 $^{\circ}$ C.

In the calculations below, you make take the density of SiC I_4 to 1.483 g cm⁻³ and the specific heat capacity of the solution to be 4.2 J $^{\circ}C^{-1}$ cm⁻³.

(i) Calculate the number of moles of silicon tetrachloride used.

Mass of SiC I_4 added = 3 x 1.483 = 4.45 g n_{SiCL} = 4.45 / (28.1 + 4 x 35.5) = 0.0262 mol

(ii) Determine the heat evolved for the above reaction between silicon tetrachloride and water.

Assume the volume change is negligible on the addition of silicon tetrachloride.

Heat evolved = mc∆T = (100) (4.2) (9.2 – 5.0) = 1760 J (3 s.f) (iii) Hence, calculate the enthalpy change of reaction, in kJ mol⁻¹.

$$\Delta \mathbf{H}_{r} = \frac{1760}{0.0262} = -67.2 \text{ kJ mol}^{-1}$$
[3]

- (c) When solid aluminium chloride is heated above 180 °C, a vapour is formed which has $M_r = 267$. When this vapour is heated above 800 °C, the vapour has $M_r = 133.5$.
 - (i) Draw the displayed formula of the vapour at 180 °C, to show its bonding.





(ii) The average M_r of the vapour is found to be 240 at 600°C. Determine the molar composition of the vapour.

Let x be the mole fraction of AlCl₃. Hence mole fraction of Al₂Cl₆ = 1 - x. x(133.5) + (1-x)267 = 240 -133.5x + 267 = 240 x = 0.202, 1 - x = 0.797

(d) Chlorine forms an oxide CI_2O_6 which exists as singly charged ions in the solid state. The oxidation states of chlorine are +5 and +7 in the cation and anion respectively. Suggest the formulae of the ions and draw the dot-and-cross diagram for the **cation**.

Formulae of ions: [CIO₂]⁺ and [CIO₄]⁻



[2]

- (e) When 100 cm³ of chlorine gas measured at room temperature and pressure is bubbled into hot aqueous sodium hydroxide solution, chlorine oxoanions are formed.
 - (i) Write the overall equation for the reaction that occurred.

 $3CI_2 + 6OH^- \rightarrow 5CI + CIO_3^- + 3H_2O$

(ii) Calculate the maximum mass of chlorine oxoanions formed.

Amount of
$$CI_2 = \frac{100}{24000} = 4.17 \times 10^{-3} \text{ mol}$$

Amount of $CIO_3^- = \frac{1}{3} \times 4.17 \times 10^{-3} = 1.39 \times 10^{-3} \text{ mol}$
Mass of $CIO_3^- = 1.39 \times 10^{-3} \times 83.5$
 $= 0.116 \text{ g}$
[3]
[Total: 16]

- 4 (a) A solution of aminoethanoic acid at its isoelectric point can act as a buffer.
 - (i) By writing appropriate equations, show how a solution of aminoethanoic acid at its isoelectric point can function as a buffer.

 $H_3N^+CH_2COO^- + H^+ \rightarrow H_3N^+CH_2COOH$ $H_3N^+CH_2COO^- + OH^- \rightarrow H_2NCH_2COO^- + H_2O$

(ii) Predict the movement of aminoethanoic acid when a potential difference is applied at pH 13.

Since the $-CO_2H$ group is deprotonated to give $-CO_2^2$, aminoethanoic acid will move towards the positive electrode.

[3]

[3]

(b) The table below shows the R groups of the various amino acids:

amino acid	aspartic acid	serine	cysteine	alanine	Lysine
abbreviation	asp	ser	cys	ala	Lys
R group	–CH ₂ CO ₂ H	–CH₂OH	–CH₂SH	$-CH_3$	– (CH ₂) ₄ NH ₂

A hexapeptide **A** has the following primary structure where aspartic acid (asp) has a free amine group:

asp-ser-cys-ala-lys-ala

(i) Draw the structural formula of hexapeptide A at pH 2.

amino acid	aspartic acid	Serine	cysteine	alanine	Lysine
abbreviation	Asp	Ser	cys	ala	Lys
R group	-CH ₂ CO ₂ H	-CH₂OH	-CH₂SH	-CH₃	- (CH ₂) ₄ NH ₂



(ii) Briefly describe the two types of R group interactions that would occur between the residues of hexapeptide A in an aqueous solution.

Any 2 of the following: <u>Ionic bond</u> between charged $-CH_2COO^2$ and $-(CH_2)_4NH_3^{\pm}$ groups. Hydrogen bond between -OH of $-CH_2COOH$ group and $-CH_2OH$ group. Disulfide bond bween –CH₂SH group of cysteine residues. Van der waals' forces between non-polar –CH₃ groups.

(iii) Describe a simple chemical test to distinguish between aqueous solutions of alanine and serine.

Add <u>acidified MnO_4^{-1} (OR acidified $Cr_2O_7^{2-}$) to each solution and <u>heat</u>.</u> Serine will decolorize the purple MnO_4^- (OR turns orange $Cr_2O_7^{2-}$ green) but alanine will not. [N.B: Na and PCI₅ NOT accepted as aqueous solutions are used.]

[6]

(c) (i) Draw a labeled diagram of the β -pleated sheet, using R as the amino acid side chain.



H-bonding clearly (at least 2), with dipoles and lone pair on O Correct projection of R groups Correct placing of NH and CO groups on each amino acid

(ii) Where, in a globular protein, will the R groups of these amino acid residues of hexapeptide A be located?

<u>-CH₂OH, -CH₂COOH, -CH₂SH and -(CH₂)₄NH₂ groups which are polar and hence hydrophilic will be located on the <u>surface</u> of the globular protein. -<u>CH₃ groups</u> which are non-polar and hence hydrophobic will be located <u>inside</u> the protein <u>away</u> from the aqueous surroundings.</u>

[4]

(d) Write an equation to show the enzymic hydrolysis of a peptide bond.

(e) A particular proteolytic enzyme **X** can hydrolyse the peptide bond between carboxyl group of cysteine and amino group of alanine of a pentapeptide to give the amino acid, cys, and two similar dipeptides, ala-cys.

Another proteolytic enzyme **Y** can hydrolyse the peptide bond between carboxyl group of alanine and amino group of cysteine to give the amino acid, cys, and two similar dipeptides, cys-ala.

Suggest the primary structure of this pentapeptide.

The primary structure of the pentapeptide is <u>cys-ala-cys-ala-cys</u>.

<u>Cysteine is before Alanine</u> since enzyme X cleaved the cys-ala peptide bond to give cys and two ala-cys.

<u>Alanine is also before Cysteine</u> since enzyme Y cleaved the ala-cys peptide bond to give two cys-ala and cys.

[2] [Total: 16]

2009 H2 Chemistry Preliminary Exams P1 Answers

Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	D	11	D	21	D	31	С
2	Α	12	С	22	D	32	С
3	Α	13	D	23	Α	33	В
4	D	14	Α	24	C	34	D
5	В	15	В	25	В	35	Α
6	Α	16	В	26	В	36	С
7	Α	17	D	27	С	37	В
8	С	18	D	28	С	38	Α
9	В	19	В	29	D	39	Α
10	В	20	Α	30	Α	40	С