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OUTSTANDING SCHOLARSHIP EXEMPLAR



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MANA TOHU MĀTAURANGA O AOTEAROA

QUALIFY FOR THE FUTURE WORLD
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Scholarship 2016 Chemistry

2.00 p.m. Monday 14 November 2016

Time allowed: Three hours

Total marks: 32

Check that the National Student Number (NSN) on your admission slip is the same as the number at the top of this page.

Pull out Resource Sheet S–CHEMR from the centre of this booklet.

You should answer ALL the questions in this booklet.

If you need more room for any answer, use the extra space provided at the back of this booklet.

Check that this booklet has pages 2–20 in the correct order and that none of these pages is blank.

You are advised to spend approximately 45 minutes on each question.

YOU MUST HAND THIS BOOKLET TO THE SUPERVISOR AT THE END OF THE EXAMINATION.

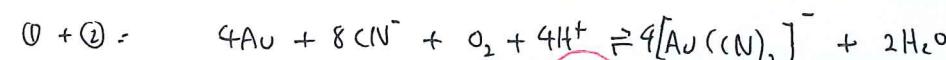
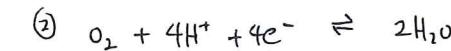
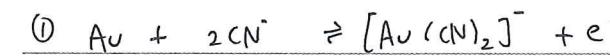
QUESTION ONE

(a) A very dilute solution of sodium cyanide, NaCN , can be used to extract gold from its ore. Gold reacts with oxygen gas to form, in the presence of cyanide ions, the $[\text{Au}(\text{CN})_2]^-$ ion. This process is carried out at pH 10–11 in order to ensure that CN^- ions are not converted to toxic hydrogen cyanide gas, HCN. The gold is then recovered as a metal by reacting the solution with zinc, which is converted to $[\text{Zn}(\text{CN})_4]^{2-}$. Sometimes the recovered gold also contains elemental silver as an impurity. This silver impurity can be removed from the gold by reacting the mixture with nitric acid.

- (i) Discuss the chemistry occurring in the extraction process described above by identifying the oxidation-reduction processes that take place, using electrode potentials to explain why gold can be extracted in this way, including the use of nitric acid to separate gold and silver.

Include balanced equations for each step in the procedure, and use the electrode potentials in the Resource Booklet to account for the reactivity observed.

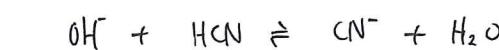
To extract gold, oxygen is used to oxidise gold to Au^{+} & $[\text{Au}(\text{CN})_2]^-$



$$\text{E}^\circ = 1.23 - (-0.60) = 1.83$$

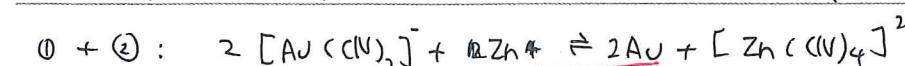
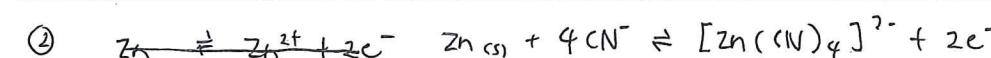
Hence at RTP reaction is thermodynamically favourable.

The reaction is done at pH 10–11. pH is a measure of the H^+ concentration in solution. Hence a high pH means that H^+ concentration is low, and OH^- concentration is high.



Hence high OH^- concentration (reduces the amount of) prevents HCN from forming in solution

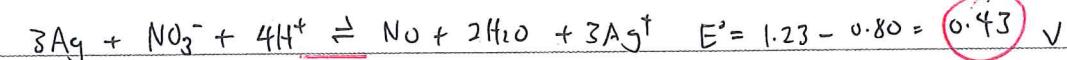
$[\text{Au}(\text{CN})_2]^-$ is reduced by Zn to form Au. Zinc is more reactive than gold.



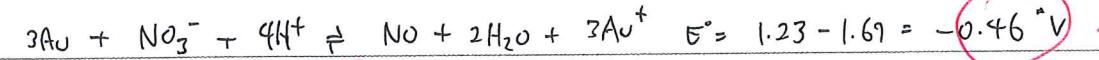
$$\text{E}^\circ = -0.60 + (-1.26) = -0.66 \text{ V}$$

Reaction is thermodynamically favourable as E° is greater than 0 //

NO_3^- formed from the dissociation of HNO_3 in solution water can act as an oxidant, oxidising Ag^{+} to Ag^{+}



However, NO_3^- is not strong enough to oxidise Au to Au^{+}



Since E° is negative, reaction is not spontaneous at room temperature.

The solid Au can thus be readily separated from the aqueous Ag^{+} , by, for example, filtration //

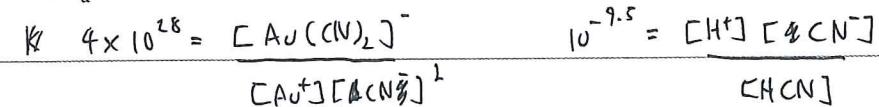
- * (ii) The stability of the complex ions $[\text{Au}(\text{CN})_2]^-$ is reflected in the size of the formation constant K_f , the equilibrium constant for the following equation:



Determine the concentration of sodium cyanide, NaCN (in mol L⁻¹) that is required to keep 99% of the soluble gold in solution as the complex ion (assume that all the soluble gold is Au(I)).

Comment on the pH dependence of the composition of the equilibrium mixture.

$$\text{pK}_a(\text{HCN}) = 9.5$$



$$\text{if } [\text{Au}(\text{CN})_2]^- = 99\%, \quad \text{Au} = 1\%$$

$$\text{hence } [\text{Au}(\text{CN})_2]^- / [\text{Au}^{+}] = 99$$

$$[\text{CN}^-]^2 = \frac{4.0 \times 10^{-9.5} \times 10^{-9.5}}{99} \quad [\text{CN}^-] = 1.99 \times 10^{-15}$$

$$[\text{CN}^-]^2 = \frac{99}{4.0 \times 10^{-9.5}} \quad [\text{CN}^-] = 4.91 \times 10^{-14} \text{ mol L}^{-1}$$

As pH decreases, H^+ and H^+ concentration decreases, the equilibrium will favour the formation of HCN: $\text{H}^+ + \text{CN}^- \rightleftharpoons \text{HCN}$

Hence the concentration of $[\text{CN}^-]$ in solution would decrease, $[\text{Au}(\text{CN})_2]^-$ would break down to Au^{+} and CN^- to reach new equilibrium

- (b) Iron ore, Fe_2O_3 , in a rock sample can be analysed by titration with acidified potassium dichromate solution, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$.

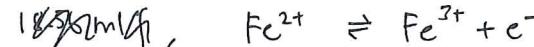
A 2.8351 g sample of haematite rock containing Fe_2O_3 , was dissolved in hot concentrated hydrochloric acid, HCl, and the solution diluted to 250.0 mL in a volumetric flask.

20.00 mL samples were pipetted into conical flasks, and a small excess of tin(II) chloride solution was added to change the colour from yellow to pale green. A saturated solution of mercury(II) chloride was then added until a small amount of white precipitate appeared. A few drops of diphenylamine sulfonate indicator were added. The resulting mixture was titrated with a standard solution of potassium dichromate. The average titre value recorded was 18.56 mL.

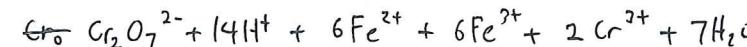
The standard solution of potassium dichromate was made by dissolving 2.5077 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in sufficient water to give 500.0 mL of solution.

- (i) Calculate the % composition of Fe_2O_3 in the haematite sample.

$$\text{Fe}_2\text{O}_3 + \text{HCl} \rightarrow 2.5077 \text{ g} \left[\frac{1 \text{ mol}}{294.2 \text{ g}} \right] \left[\frac{1000 \text{ mL}}{500 \text{ mL}} \right] = 0.0170 \text{ mol L}^{-1}$$



When the tin is added, the Fe^{2+} in solution is reduced to Fe^{2+} , hence producing a green solution. When dichromate is added, the Fe^{2+} is oxidized back to Fe^{3+} .



$$18.56 \text{ mL} \left[\frac{0.0170 \text{ mol}}{1000 \text{ mL}} \right] \left[\frac{6 \text{ mol Fe}^{2+}}{1 \text{ mol Cr}_2\text{O}_7^{2-}} \right] \left[\frac{1 \text{ mol Fe}_2\text{O}_3}{6 \text{ mol Fe}^{2+}} \right] \left[\frac{159.8 \text{ g}}{1 \text{ mol Fe}_2\text{O}_3} \right] = 0.181 \text{ g in } 250 \text{ mL}$$

$$0.181 \text{ g} \left[\frac{250 \text{ mL}}{20 \text{ mL}} \right] = 1.89 \text{ g of } \text{Fe}_2\text{O}_3$$

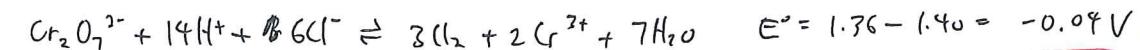
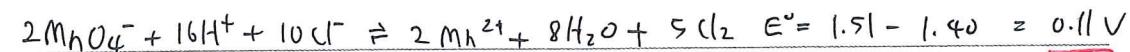
$$\frac{1.8908}{2.8351} \times 100 = 66.7 \%$$

N.R. $m(\text{K}_2\text{Cr}_2\text{O}_7) = 2 \times 39.1 + 52 \times 2 + 7 \times 16 = 294.2 \text{ g/mol}$

$$m(\text{Fe}_2\text{O}_3) = 55.9 \times 2 + 3 \times 16 = 159.8 \text{ g/mol} //$$

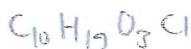
- (ii) Explain why it is not appropriate to carry out this titration using potassium permanganate, KMnO_4 , instead of potassium dichromate, as the oxidant.

MnO_4^- has a larger E° value than $\text{Cr}_2\text{O}_7^{2-}$, hence MnO_4^- is a stronger oxidant than $\text{Cr}_2\text{O}_7^{2-}$. MnO_4^- strong enough to oxidise Cl^- to form Cl_2 , hence the results of the titration would not be accurate for determining the Fe^{2+} concentration in solution.



Reaction between $\text{Cr}_2\text{O}_7^{2-}$ and Cl^- is not thermodynamically favourable. The excess K MnO_4^- may also oxidise the $\text{Ti}^{(II)}$ in solution //

QUESTION TWO



- (a) Compound A, has the molecular formula $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Cl}$ and has one chiral centre. Compound A does not decolourise bromine water. When Compound A is reacted with dilute acid solution, two products, Compound B and Compound C, are formed.

Compound B does not have a chiral centre. When subjected to mass spectrometry, it is found to have a molecular ion peak at $m/z = 114$.

Compound C, when subjected to mass spectrometry, is found to have a molecular ion peak at $m/z = 108$. There is also a $M+2$ peak present, and the ratio of the heights of the M and $M+2$ peaks is 3:1. C_1

When Compound C is treated with thionyl chloride, SOCl_2 , Compound D is produced.

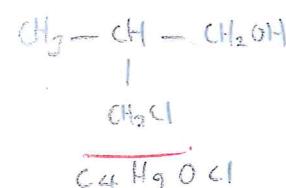
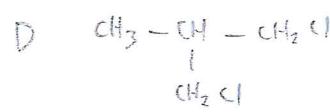
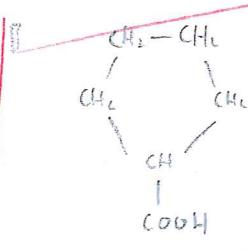
The ^{13}C NMR spectrum of all Compounds A to D are available in the Resource Booklet.

The IR spectrum of Compound B is also available.

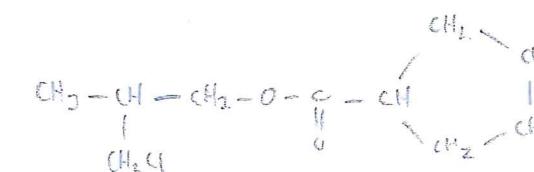
Determine the identity of Compounds A to D.

Justify your answers by linking your choices to the spectra provided and the information given above.

Compounds A to D:



PENCIL



A

Justifications: When dilute acid is added to A, A breaks down into two is hydrolyzed

A breaks into two products. Hence A must be an ester,

For B, the peak at 180 in ^{13}C NMR shows that it is a carboxylic acid.

By deduction, C must be an alcohol. (which is confirmed by the peak at 67 ppm)

Since B is not saturated, but does not contain a double or triple bond, ($=\text{H}$ doesn't decolorise bromine water) it must be a cyclic compound

B only have four different environments on its carbon, hence it must contain a C_5 ring. (it only has 4 peaks in ^{13}C NMR).

The $M+2$ peak in C shows that it contains a chlorine atom,

but possibly contains a halogen. The 3:1 ratio confirms that the

halogen is a chlorine atom. It has only one chiral center, hence, the

hydroxyl and chlorine must be attached to the same carbon

The peak at ≈ 48 ppm is caused by $\text{C}-\text{Cl}$, and the peaks at 14 and 37 are caused by alky groups.

Attututing that Looking at the ^{13}C spectrum of D, the OH peak disappears that replaced by a peak at 50. This is the sum of the p height of the other two peaks. Hence SOCl_2 replaces OH with Cl, such that only three environments for carbon remain

The other two peaks remain in approximately the same position

^{13}C of A shows that only 8 environments exist for the 10 carbon

A chiral carbon is a carbon with four different functional groups attached to it. The ratio of 10 carbon to 17 hydrogens show that compound

A has at least 2 digits of //

- (b) Nitrogen dioxide, NO_2 , is a brown gas that is often a component of air pollution. It is in equilibrium with a dimeric species, dinitrogen tetroxide, N_2O_4 . Dinitrogen tetroxide is used as a rocket fuel in combination with hydrazine, N_2H_4 , and the products of the combustion reaction of this mixture are gaseous nitrogen and water.

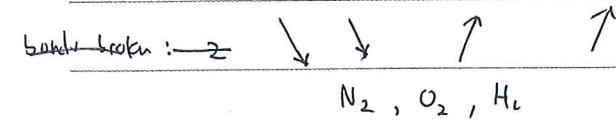
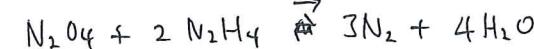
Table 1: Selected thermochemical data

Chemical	Enthalpy of formation/kJ mol ⁻¹	Boiling point/°C
NO_2	33.2	21
N_2O_4	9.2	(21)
N_2H_4	50.6	(114)
N_2	0	-196
H_2O	-286	100

?

- * (ii) Discuss why a $\text{N}_2\text{O}_4 / \text{N}_2\text{H}_4$ mixture is suitable for use as a rocket fuel, linking appropriate data from Tables 1 and 2 to molecular structures.

① A fuel must release energy when combustion.



$$\Delta H_f: \text{using Hess's law: } = \Delta H_f(\text{N}_2\text{O}_4) - 2\Delta H_f(\text{N}_2\text{H}_4) + 3\Delta H_f(\text{N}_2) + 4\Delta H_f(\text{H}_2\text{O})$$

$$\Delta H_f = -9.2 - 2(50.6) + 3(0) + 4(-286)$$

$$= -1254.4 \text{ kJ}$$

The combustion of the mixture is exothermic, hence releases energy to power the movement of the rocket.

② The fuel produces two products: N_2 and H_2O , which are stable and easy to store. They do not pose any threats to the crew people on board the rocket. This is shown by the large bond enthalpy of

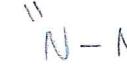
③ $\text{N} \equiv \text{N}$ (945 kJ mol^{-1})

④ N_2O_4 , NO_2 and N_2H_4 have relatively high boiling points, hence can be stored as liquids quite easily. Storing fuel as liquid saves space because liquid has a much higher density than gas. At 0°C , both N_2O_4 and N_2H_4 will be liquids.

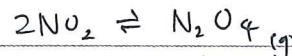
Table 2: Selected bond enthalpies (kJ mol⁻¹)

N-N (N_2)	945
N-N (N_2O_4)	57
N-N (N_2H_4)	298

O-H (H_2O)	499
N-O (NO_2)	305
N-H	391



- (i) Discuss how enthalpy and entropy affect the dimerisation equilibrium.



Reactions are driven by two forces: to obtain lower energy state, and to achieve greater increase the entropy / disorder.

Bond formation is exothermic process, hence the forward reaction (formation of N-N bond in N_2O_4 is -57 kJ mol^{-1}), since heat is released to the surrounding, the react N_2O_4 is more in a lower energy state - more stable than NO_2 .

In terms of enthalpy, forward reaction is favourable. Entropy, on the other hand, is a measure of the different ways in which we can arrange the molecules in a system. The greater the number of molecules, the more ways we can arrange these molecules, and the greater the states disorder.

For: In the forward reaction, 2 molecules react to form 1 molecule, hence entropy decreases. In terms of entropy, the reverse reaction is favourable. According to the Gibbs equation, equilibrium will be reached when $\Delta G = 0$, hence $\Delta H = T\Delta S$. at equilibrium.

n/

s/

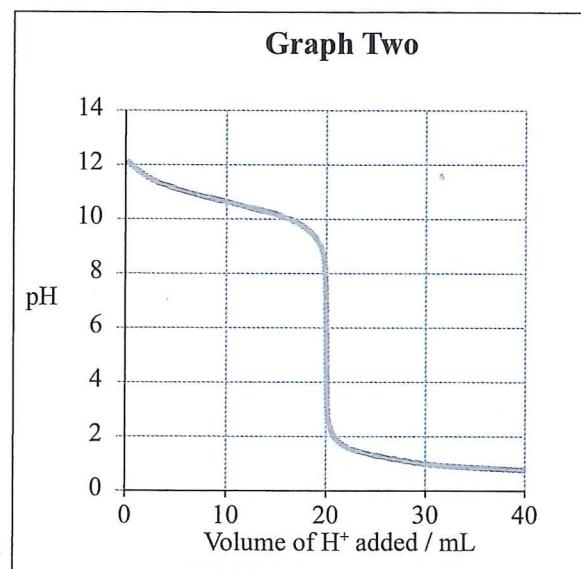
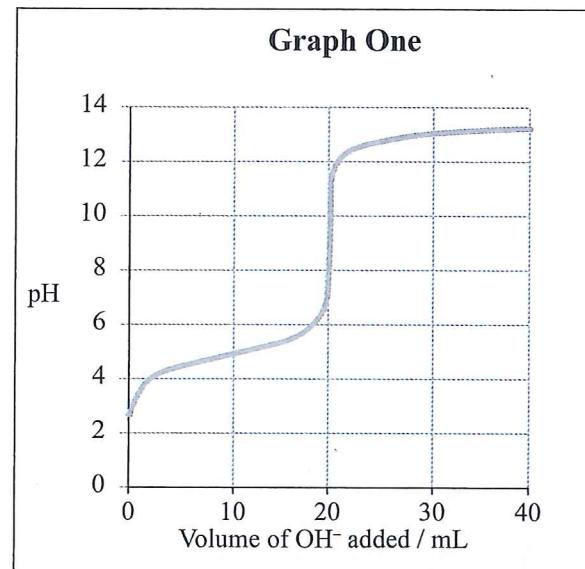
QUESTION THREE

- (a) The pH titration curves for the following reactions are shown below.

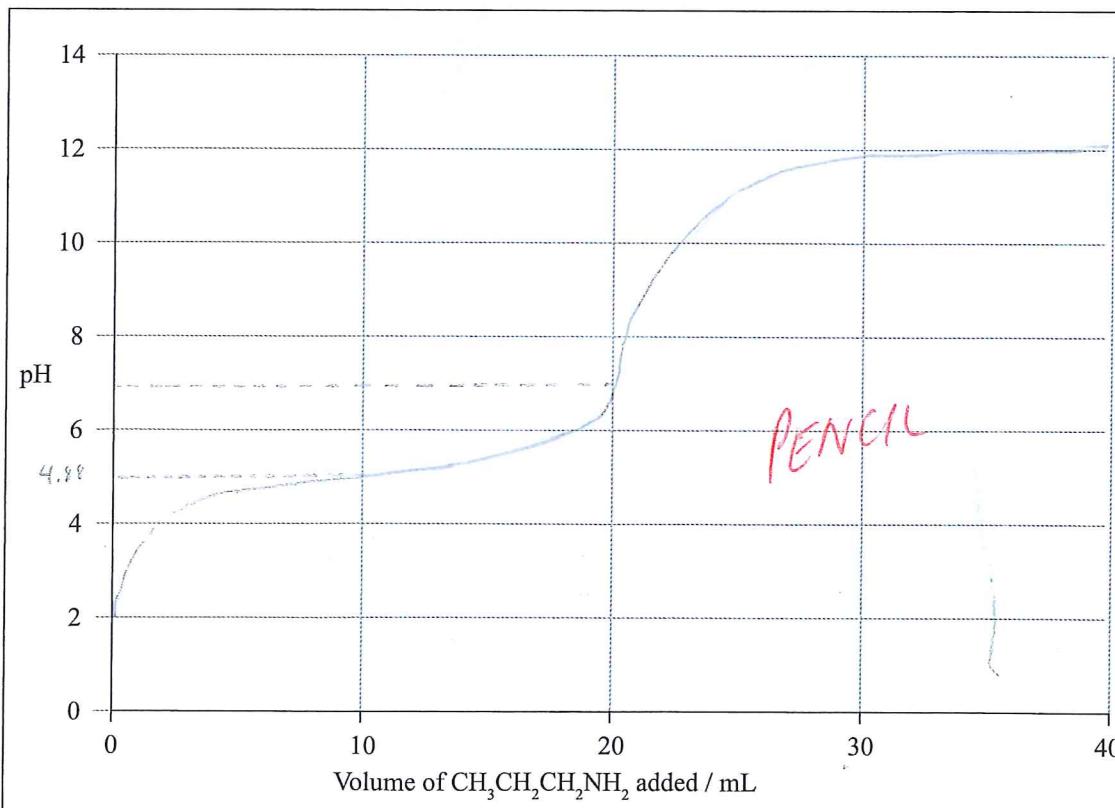
20 mL of 0.5 mol L⁻¹ propanoic acid, CH₃CH₂COOH, titrated with 0.5 mol L⁻¹ sodium hydroxide (Graph One)

20 mL of 0.5 mol L⁻¹ propan-1-amine, CH₃CH₂CH₂NH₂, titrated with 0.5 mol L⁻¹ hydrochloric acid (Graph Two)

$$pK_a(\text{CH}_3\text{CH}_2\text{COOH}) = 4.88 \quad pK_a(\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_3^+) = 10.71$$



- * (i) Sketch the titration curve for the reaction of 20 mL of 0.5 mol L⁻¹ propanoic acid, CH₃CH₂COOH, titrated with 0.5 mol L⁻¹ propan-1-amine, CH₃CH₂CH₂NH₂.

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- (ii) Aqueous solutions containing equal concentrations of propanoic acid and propan-1-amine are mixed.

Complete the table below by giving the **dominant** species that would be present in the mixture at the given pH.

Give reasons linked to the graphs, and show relevant equations.

pH	1	8	13
Dominant species	CH ₃ CH ₂ COO ⁻ CH ₃ CH ₂ CH ₂ NH ₃ ⁺	CH ₃ CH ₂ COO ⁻ CH ₃ CH ₂ CH ₂ NH ₃ ⁺ CH ₃ CH ₂ COO ⁻	CH ₃ CH ₂ COO ⁻ CH ₃ CH ₂ CH ₂ NH ₂

pKa is the pH when half of the acid is neutralised, hence at pH=pKa

[A⁻] = [HA]. At pH=8 is less than

since $k_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$ if $[\text{A}^-] > [\text{HA}]$ $p[\text{H}^+] > pK_a$, $[\text{HA}] > [\text{A}^-]$

if $p[\text{H}^+] < pK_a$, if if $pK_a < \text{pH} > pK_a$, the dominant form must be A⁻, if pH < pKa, dominant form must be HA.

At pH=1, pH=1 is less than both pKa of CH₃CH₂COOH can pKa of CH₃CH₂CH₂NH₃⁺, hence the dominant species must be the conjugate acid.

pH=8, is less greater than pKa of CH₃CH₂COOH, hence dominant form is conjugate base CH₃CH₂COO⁻, but less than pKa of

propan-1-amine, hence the conjugate acid CH₃CH₂CH₂NH₃⁺ must still be be the dominant form. pH 13 is larger than both pKa. pKa, hence the dominant form must be the conjugate base.

Graph At pH 1, the graph on show that CH₃CH₂COOH has not yet between half neutralised, while graph 2 shows that all the CH₃CH₂CH₂NH₂ has been neutralised to CH₃CH₂CH₂NH₃⁺.

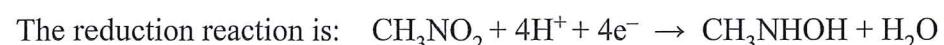
At pH 8, graph 1 shows that most of the CH₃COOH has been neutralised

$$-\log k_a = \log \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

$$\log pK_a = \log [\text{H}^+] +$$

- (b) An organic nitro-compound, CH_3NO_2 , is reduced by electrolysis in an aqueous ethanoate buffer solution at pH 5.0. In the solution, the total ethanoate concentration, $[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$ is known to be 0.500 mol L⁻¹.

A 300 mL sample of the buffered solution contains 0.0100 mol L⁻¹ CH_3NO_2 that has been completely reduced by the electrolytic process.



- (i) Calculate the pH of the solution after reduction of CH_3NO_2 is complete.

Assume that the effect of the hydrolysis of the methylhydroxylamine, CH_3NHOH , is negligible at this pH.

$$K_a(\text{CH}_3\text{COOH}) = 1.75 \times 10^{-5} \quad pK_a(\text{CH}_3\text{COOH}) = 4.76$$

$$K_a = \frac{[\text{H}^+] [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad , \quad x = [\text{CH}_3\text{COO}^-]$$

$$300 \text{ mL} \left[\frac{0.01 \text{ mol}}{1000 \text{ mL}} \right] \left[\frac{4 \text{ mol H}^+}{1 \text{ mol } \text{CH}_3\text{NO}_2} \right] = 0.012 \text{ mol L}^{-1} \text{ H}^+ \text{ reacted with } \text{CH}_3\text{NO}_2$$

$$0.012 \left[\frac{1000 \text{ cm}^3}{300 \text{ cm}^3} \right] = 0.04 \text{ mol dm}^{-3}, \quad \text{H}^+ \text{ ions must be provided by } \text{CH}_3\text{COOH}$$

$$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$$

hence if original concentration to x of CH_3COOH is x , after reaction

$$\text{its concentration is } x - 0.04 \text{ mol dm}^{-3}, \quad [\text{CH}_3\text{COO}^-] = 0.5 - (x - 0.04)$$

$$= 0.54 - x$$

$$\frac{0.5 - x}{x} \cdot 10^{-5} = \frac{0.54 - x}{x - 0.04} \cdot [\text{H}^+] \quad [\text{H}^+] = \frac{10^{-5} \cdot (0.5 - x)(x - 0.04)}{x(0.54 - x)}$$

$$10^{-5} (0.5x - x^2 - 0.02 + 0.04x) = [\text{H}^+] (0.54x - x^2)$$

$$10^{-5} K_a = \frac{10^{-5} (0.5 - x)}{x} = 1.75 \times 10^{-5}$$

$$0.5 \times 10^{-5} - x \times 10^{-5} = 1.75x \times 10^{-5}$$

$$0.5 \times 10^{-5} = 2.75x \times 10^{-5}$$

$$\frac{0.5}{2.75} = x = 0.181818 \approx 0.182 \text{ mol dm}^{-3}$$

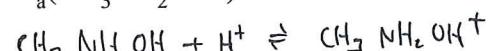
$$[\text{H}^+] = \frac{10^{-5} (0.5x - x^2 - 0.02 + 0.04x)}{(0.54x - x^2)}$$

$$= 0.693 \times 10^{-5} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}^+] = 5.16 //$$

- (ii) Evaluate the validity of the assumption that hydrolysis of methylhydroxylamine does not occur at this pH.

$$K_a(\text{CH}_3\text{NH}_2\text{OH}^+) = 1.09 \times 10^{-6} \quad pK_a(\text{CH}_3\text{NH}_2\text{OH}^+) = 5.96$$



$$\frac{[\text{CH}_3\text{NH}_2\text{OH}][\text{H}^+]}{[\text{CH}_3\text{NH}_2\text{OH}^+]} = 1.09 \times 10^{-6}$$

let $[\text{H}^+] = 0.693 \times 10^{-5} \text{ mol L}^{-1}$ obtained from part (i)

$$\frac{[\text{CH}_3\text{NH}_2\text{OH}]}{[\text{CH}_3\text{NH}_2\text{OH}^+]} = \frac{1.09 \times 10^{-6}}{0.693 \times 10^{-5}} = 0.157$$

so it appears that at pH 5.6, most of the species in solution

is $\text{CH}_3\text{NH}_2\text{OH}^+$ the concentration of $\text{CH}_3\text{NH}_2\text{OH}^+$ is larger than $\text{CH}_3\text{NH}_2\text{OH}$. Hence we cannot make the assumption that the

hydrolysis of methyl hydroxylamine does not occur or is negligible //

QUESTION FOUR

The melting points of a selection of hydrides are given in the table below. The position of the hydrides in the table reflects the relative position of the non-hydrogen element in the Periodic Table.

Period	1	2	13	14	15	16	17
1							
2				CH_4 -182°C	NH_3 -78°C	H_2O 0°C	HF -83°C
3				SiH_4 -185°C	PH_3 -133°C	H_2S -86°C	
4					AsH_3 -116°C	H_2Se -66°C	
5					SbH_3 -88°C	H_2Te -49°C	

- * (a) (i) Discuss the variation in the melting points of the hydrides of the elements of Period 3 (SiH_4 , PH_3 , and H_2S).

Melting point of group 3 hydrides increase across the group. It appears

All three are either liquids or gas at room temperature

Melting The increase appears to be fairly linear, approximately +50°C per proton. Melting point is a measure of the strength of the intermolecular forces. This means that H_2S has the strongest intermolecular forces while SiH_4 has the least. Since all three have the same electron configuration around the central atom (complete octet), the total number of electrons are the same, hence the difference in the strength of the van der Waals forces is small and would not explain the significant difference in boiling point.

However, since the central number of control protons in the central atom of the hydride increase across the group, the central atom would attract the bonded electrons more strongly; in other words, their electronegativity increases across the group. Unlike SiH_4 , PH_3 and H_2S are not symmetrical. Hence due to their highly electronegative central atom, the atom electrons would be pulled away from the

less electronegative hydrogen atoms, forming polar products a permanent uneven distribution of electrons in the electron cloud. The size here a dipole. These dipoles can attract other dipoles, hence H_2S across the group, the strength of the dipole-dipole interaction increase because stronger than, hence boiling point increase //

- (ii) Discuss the trend in the melting points of the hydrides of the elements of Group 15 (NH_3 to SbH_3).

General trend is that down the group the size of the melting point increases. This is because the total number of electrons in the molecule increases, hence the molecule becomes more polarizable down the group.

There's a higher probability of having the molecule having an uneven distribution of electrons in the electron cloud, hence the higher chance of forming instantaneous dipoles. This is supported by table: PH_3 has melting point of -133°C, AsH_3 is -116°C, SbH_3 is -88°C, showing an increasing melting point. However, NH_3 does not fit this trend. NH_3 has an abnormally high melting point of -78°C. This is because NH_3 - Nitrogen is highly electronegative. It draws electrons away from hydrogen, so that the nitrogen has a high electron density than hydrogen. Nitrogen gains a slight positive charge, allowing it to form hydrogen bonds with the slightly positive hydrogen atoms on other NH_3 molecules. Thus the hydrogen bonding is the strongest form of intermolecular forces //

Question Four continues
on the following page.

- (iii) The acidic properties of the non-metal hydrides increase left to right across a period, and down a group.

Account for these trends using the hydrides of Period 2 elements (CH_4 to HF) and those of Group 16 elements (H_2O to H_2Te).

Acidic characteristic increases across the group because the electronegativity of the central atom increases. The $\text{X}-\text{H}$ bond would become more polar as the electronegativity increases, hence it will be more likely to break heterolytically, giving both electrons & in the form to central metal & form an product H^+ . Hence in period two CH_4 is neutral, NH_3 is a base, H_2O is neutral both but is amphoteric (hence can be dissociate to produce H^+), and HF is a weak acid. HF is a stronger acid than H_2O because F is more electronegative than O, hence H-F bond dissociates more easily than the H-O bond.

Down the group 16, the size of the central metal atom increases. Hence the attraction between the atom and the hydrogen decreases down the group. As the bond strength decreases, the $\text{X}-\text{H}$ bond, where X is a group 16 atom, decreases in bond strength and can dissociate more readily in solution to form H^+ .

- (b) The hydrides of the elements of Groups 1 and 2 are all solids at room temperature, but apart from LiH , which melts at 689°C , the metallic hydrides decompose at temperatures around 250°C . Because of this it is not possible to use melting points to compare the strength of the metal hydride bond. To compare the strength of these bonds, some enthalpy data is provided in the table below.

Note: Lattice enthalpy is the standard enthalpy change for the conversion of an ionic solid into a gas of ions.

	Δ_f^H / kJ mol^{-1}	Lattice enthalpy / kJ mol^{-1}
LiH	-90.65	912.5
NaH	-56.4	845.7
KH	-57.8	741.9

	Δ_f^H / kJ mol^{-1}	Lattice enthalpy / kJ mol^{-1}
MgH_2	-75.2	2721
CaH_2	-186	2458

Compare and contrast the expected strength of the metal hydride bonds of the Group 1 and 2 elements, and justify whether the lattice enthalpy data or the enthalpy of formation data is the better predictor of the expected trends in the strength of the metal hydride bonds.

The lattice enthalpy is the energy required to completely separate all the ions in an ionic lattice. The data show that the group 2 metal hydrides have require more energy to separate. Lattice enthalpy of MgH_2 is 2721 kJ mol^{-1} and for CaH_2 it's 2458 , while lattice energy of LiH , NaH and KH are 912.5 , 845.7 , 741.9 respectively, approximately to $\frac{1}{3}$ of the group 2 hydrides. The strength of the metal hydride data also reveals a second trend: the strength of the metal hydride bonds decreases down the group.

Enthalpy of formation is the energy change when one mole of an ionic lattice is formed from its constituent elements in their standard state. Unlike the lattice enthalpy, it includes the energy required to break not only contains the energy released when the ions form ionic bonds, it also includes the energy needed to break the metallic lattice of the metal and the energy required to separate H^+ bonds. Hence the enthalpy of formation should not give an accurate predictor of the strength of the metal hydride bonds.

In group 1, the enthalpy of formation decreases down the group becoming less negative down the group. (from -90.65 to -56.4 and then -57.8)

In group 2 the enthalpy of formation becomes more negative down the group (from $-75.2 \text{ kJ mol}^{-1}$ for MgH_2 to -186 kJ mol^{-1} for CaH_2). Since the charge density of the metal ion decreases down the group, the (the charge = metal hydride bond cannot be increasing in strength down the group) Hence it appears that enthalpy of formation would not be a good indicator of bond metal hydride bond strength.

From data, the expected strength of group II hydride is greater than that of group I hydride. Group II metal ions have $+2$ charge instead of $+1$ for group I ions, hence using cation column law, we would expect the electrostatic attraction between $2+$ ion and H^- to be stronger than

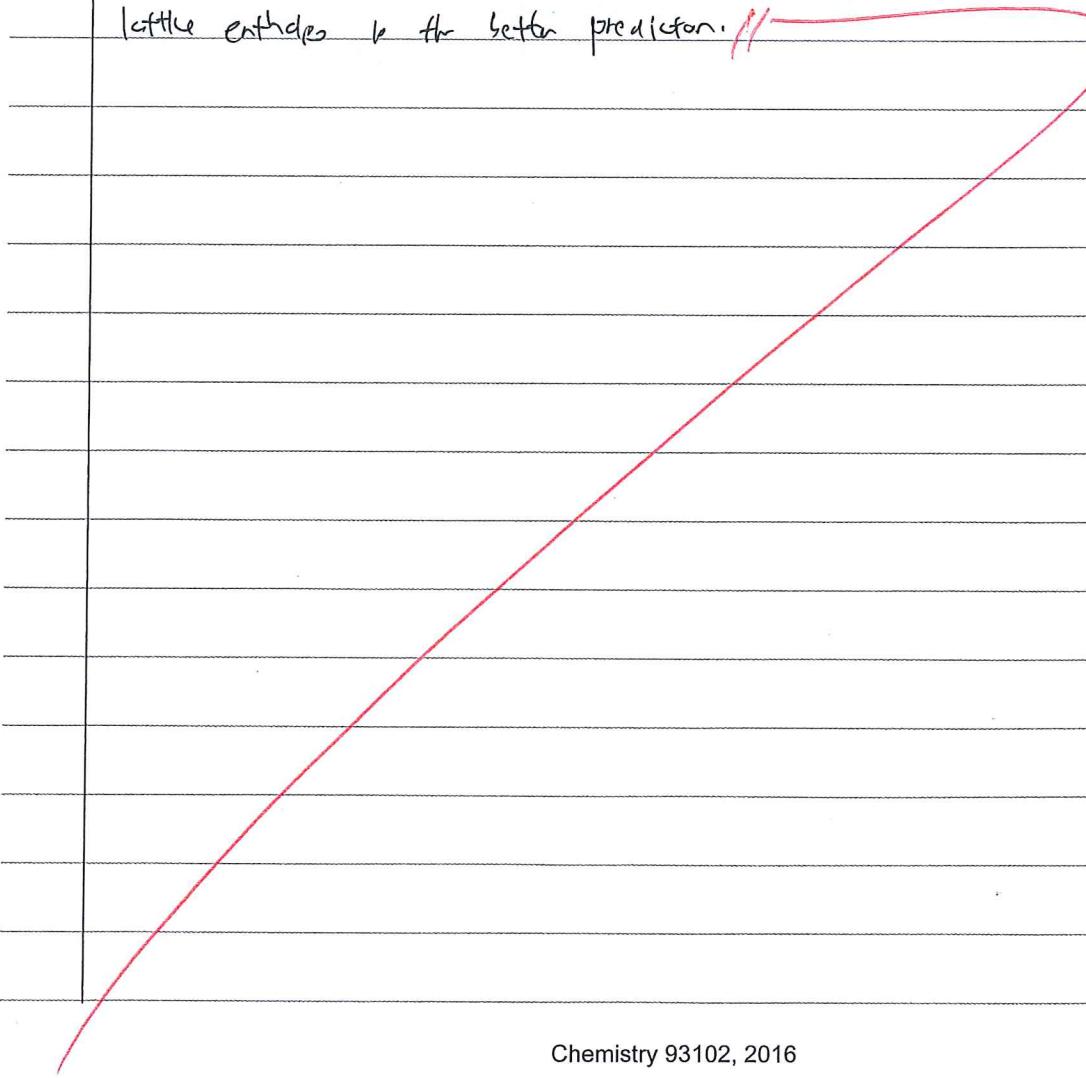
QUESTION
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(f)(iii)(b) that between group I metal ions and H^+ . (coulomb's law states that the force between two charges is proportional to the product of their charges and inversely proportional to their distance apart squared.) Furthermore, group II atoms lose two electrons to form $+2$ ions, hence group II metal ions are smaller than group I ions, & since σ hence they will have a larger charge density. This would mean that bond strength between X^{2+} and H^- would be expected to be stronger than that between X^+ and H^- . But we would expect attraction to decrease down the group. This is because the net ion charge on the ion decreases between constant, but their ionic radius increases as atoms gain more electron orbitals down the group or the valence electrons become further away from the nucleus.

The data of the lattice enthalpy supports the model, hence lattice enthalpies is the better prediction.


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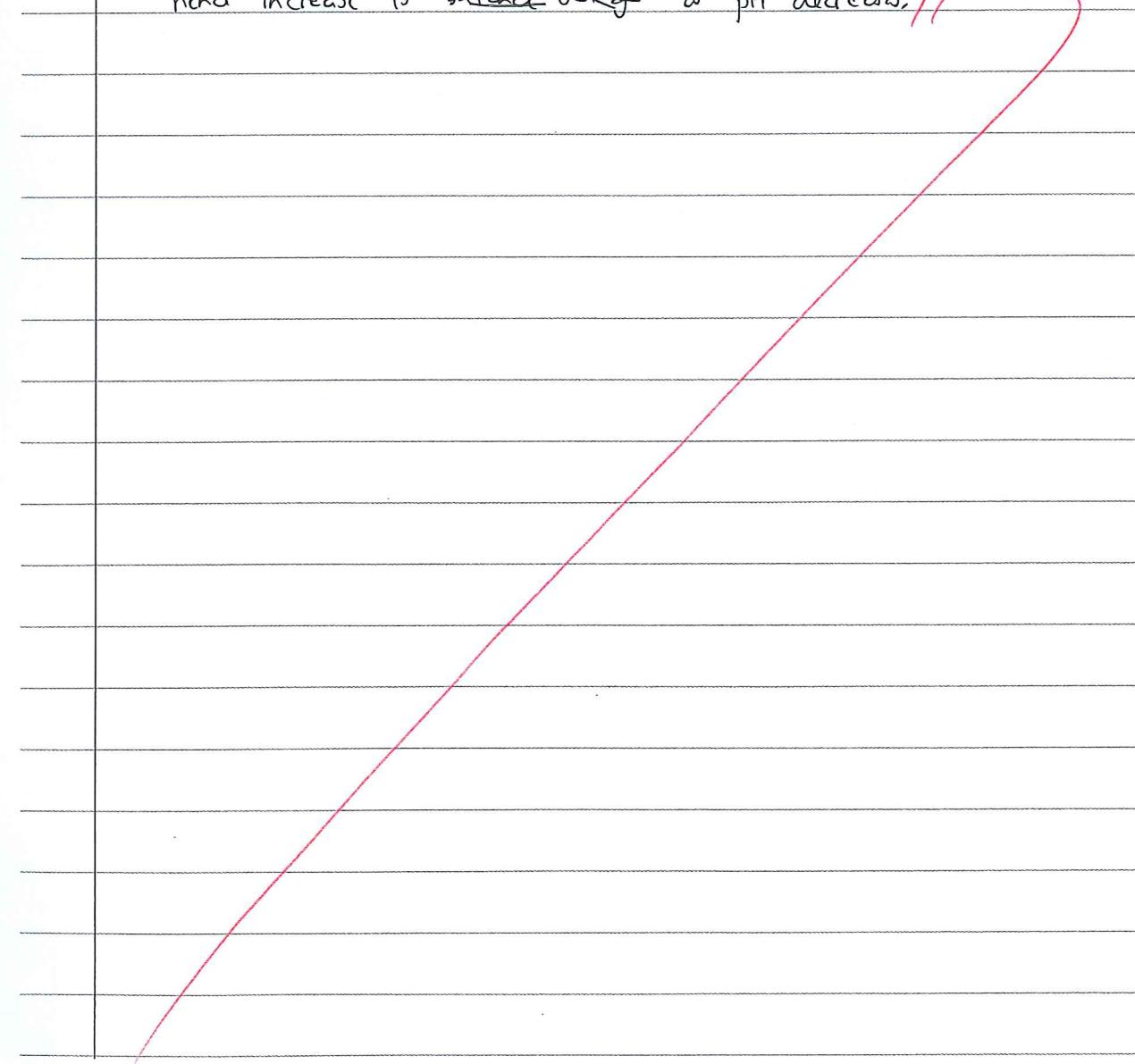
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$$1. \text{ (ii)} \Delta K_a = \frac{[H^+][CN^-]}{[HCN]} \quad K = \frac{[Au(CN)_2^-]}{[Au^+][CN^-]^2}$$

seen.

As pH it decreases, the concentration of free H^+ ions in solution will increase. To remain at equilibrium, the concentration of CN^- must decrease. The concentration of HCN remains is much larger than either $[H^+]$ or $[CN^-]$, hence we can assume it to remain roughly constant. Since $[CN^-]$ decreases, we would expect $[Au^+]$ to increase. $[Au(CN)_2^-]$ is much larger than either $[Au^+]$ or $[CN^-]$ hence we can assume it to be constant. $[Au^+]$ concentration must hence increase to balance out of a pH decrease. //

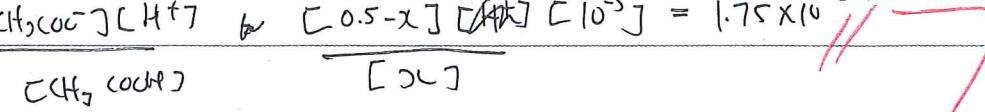


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3 (i) $k_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \Rightarrow \frac{[0.5-x][10^{-5}]}{[x]} = 1.75 \times 10^{-5}$



93102

Outstanding Scholarship paper – Total score = 30.

Q	Score	Annotation notes
1	7	<p>The candidate has analysed the provided information and given a coherent description of the relevant chemistry, supported by equations. The calculation is clearly set out and shows logical thinking. The candidate has reflected on the question and planned a succinct answer that integrates chemistry vocabulary and symbols. In part (a)(i), the candidate identified key oxidation-reduction processes taking place, has given equations, and calculated electrode potentials for them (albeit, with some errors).</p> <p>In part (a)(ii), the candidate determined the concentration of sodium cyanide and commented on the pH dependence of the composition for the equilibrium mixture.</p> <p>In part (b)(i), the candidate correctly calculated the percentage composition of iron ore in the haematite sample.</p> <p>In part (b)(ii), the candidate has explained why dichromate is used in the titration but not permanganate; and supported their answer with equations, including related E° calculations.</p>
2	7	<p>The candidate has analysed the information and data provided, and applied their own knowledge to solve the given problem. Their answer is fluent and coherent and relevant to the problem and data given.</p> <p>In part (a), the structures for compounds A, B, C & D are correct, complete with justification for their identification.</p> <p>In part (b), enthalpies for reactions in both parts (i) and (ii) are correct and some discussion of enthalpy and entropy changes is given.</p>
3	8	<p>The candidate has shown sophisticated integration and abstraction using the information given and their own knowledge. They have given very succinct answers supported by symbols and chemistry vocabulary. Calculations are clearly set out and follow a logical order, reflecting a high level of planning and processing of the information given.</p> <p>In part (a)(i), the candidate sketched an appropriate titration curve for the weak acid / weak base titration.</p> <p>In part (a)(ii) the candidate has identified the dominant species with concise justifications.</p> <p>In part (b), the final pH of the solution is correctly calculated, with clear working. The candidate also evaluated the validity of the assumption clearly.</p>
4	8	<p>The candidate has demonstrated convincing communication; answers are clear and integrate information from the question and incorporate given data in a logical manner. They have identified relevant information and analysed it to address the questions.</p>