ST ANDREW'S JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATIONS

HIGHER 2

CANDIDATE NAME

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CLASS

CHEMISTRY 9729/02

Paper 2 Structured Questions **31 August 2022**

Candidates answer on the Question Paper. **2 hours**

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work that you hand in.

Write in dark blue or black pen.

You may use a HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the **spaces provided** on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use		
Q1		**12**
Q2		**14**
Q3		**14**
Q4		**10**
Q5		**25**
Total		**75**

This document consists of **XX** printed pages (including this cover page).

1 Hydrazine, N_2H_4, is a colourless liquid with an ammonia-like odour. It is an important precursor in the pharmaceuticals industry.

(a) Hydrazine exists as a liquid while ammonia exists as a gas at room temperature and pressure. State two reasons to explain this difference in physical state. **[2]**

Both ammonia and hydrazine are polar simple covalent molecules, capable of forming intermolecular hydrogen bonds. Hydrazine has more hydrogen bonding sites and therefore, it is able to form **more extensive** **intermolecular hydrogen bonds**. At the same time, it has **more electrons / larger electron cloud size** and this leads to **stronger intermolecular instantaneous dipole-induced dipole interactions**. Hence, both of these require more energy to overcome.

(b) The K_b values of hydrazine, ethylamine, and phenylamine are shown in **Table 1.1**.

Table 1.1

base	K_b / mol dm^{-3}
Hydrazine	1.7×10^{-6} (for K_{b1})
Ethylamine	4.5×10^{-4}
Phenylamine	7.4×10^{-10}

(i) Explain what is meant by the term *Bronsted-Lowry base*. **[1]**

A Bronsted-Lowry base refers to a **proton acceptor**.

(ii) Explain the relative magnitudes of the K_b values in **Table 1.1**. **[2]**

(most basic) **ethylamine > hydrazine > phenylamine**

Unlike hydrazine, ethylamine has an **electron donating alkyl/ethyl group** which makes the **lone pair of electrons on N more available to accept H^+**.

Phenylamine is weaker base than hydrazine as the **lone pair of electrons on N is delocalised into the benzene ring**, making it **less available to accept H^+**.

(iii) The K_b values of diethylamine and triethylamine are shown in **Table 1.2**.

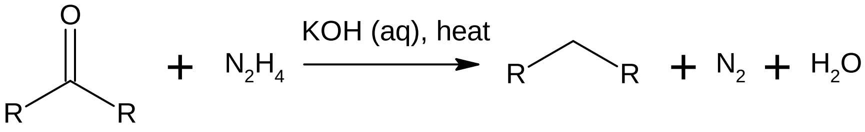
Table 1.2

base	K_b / mol dm^{-3}
Diethylamine	6.9×10^{-4}
Triethylamine	6.5×10^{-5}

Suggest why the K_b value of triethylamine is significantly smaller than the K_b values of ethylamine and diethylamine. **[1]**

Triethylamine is a tertiary amine and the **presence of (one) more R/alkyl groups will result in steric hindrance**, thus leading to a smaller extent of base dissociation in aqueous / less likely to accept a H^+.

(c) The Wolff-Kishner reaction is a valuable synthetic method to convert carbonyl compounds into alkanes. This is done by reacting a carbonyl compound with excess hydrazine in the presence of potassium hydroxide.

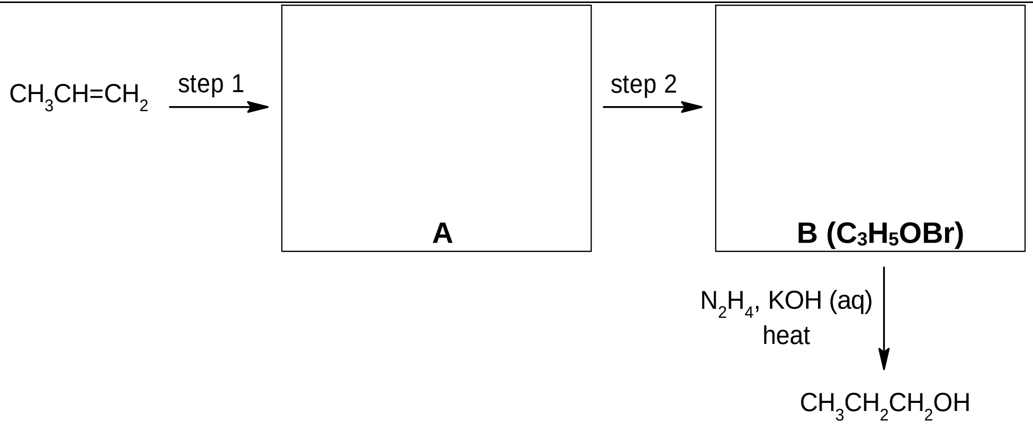


(i) Suggest a simple chemical test to monitor the completion of the Wolff-Kishner reaction. **[2]**

Add **2,4-dinitrophenylhydrazine / 2,4-DNPH** to the reaction mixture (and warm)

If the reaction was complete, there will be **no orange ppt**.

(ii) Propan-1-ol can be synthesised from propene by the following 3-step route that incorporates the Wolff-Kishner reaction.



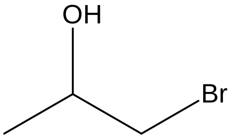
Suggest the structures of intermediate products **A** and **B** and state the reagents and conditions for each step. **[4]**

Reagents and conditions

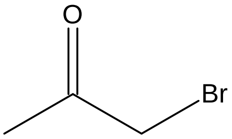
Step 1: . . . .

Step 2: . . . .

A:



B:



Reagents and conditions

Step 1: **$Br_2(aq)$**

Step 2: **$K_2Cr_2O_7(aq)$ or $KMnO_4(aq)$, $H_2SO_4(aq)$, heat**

[Total: 12]

2	Organic matter is known to decay under low oxygen conditions, such as in swamps. The sulfate-reducing bacteria present in the organic matter will reduce the various sulfates into hydrogen sulfide, H_2S. Some of the hydrogen sulfide will react with Fe^{2+} present in swamp to produce insoluble FeS, which is responsible for the brown colour of sludge in the swamp. **reaction 1** $H_2S(g) + aq \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$ **reaction 2** $Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$ $\Delta H^{\ominus}_{ppt}$			
	(a)	**(i)**	In a saturated solution of hydrogen sulfide, $[H^+]^2[S^{2-}]$ is 1.0×10^{-23} mol^3 dm^{-9}. Calculate the maximum concentration of sulfide ions present in the swamp, given that the pH of swamp water is 6.8.	**[1]**
			$[H^+] = 10^{-6.8}$ $= 1.5848 \text{ X } 10^{-7}$ mol dm^{-3} $[S^{2-}] = \frac{1 \times 10^{-23}}{[1.5848 \times 10^{-7}]^2} = \underline{\mathbf{3.98 \times 10^{-10}}}$ mol dm^{-3}	
		(ii)	Hence, calculate the minimum concentration of Fe^{2+} in the swamp required for the precipitation of FeS. (K_{sp} of FeS = 4.9×10^{-18} mol^2 dm^{-6})	**[1]**
			Ecf from (a)(i) $K_{sp} = [Fe^{2+}][S^{2-}]$ $[Fe^{2+}] = \frac{4.9 \times 10^{-18}}{3.981 \times 10^{-10}} = \underline{\mathbf{1.23 \times 10^{-8}}}$ mol dm^{-3}	
		(iii)	$\Delta G^{\ominus}_{ppt}$, can be determined by using the following expression, where R is the molar gas constant and T is the temperature measured in K. $\Delta G^{\ominus}_{ppt} = 2.303RT \lg K_{sp}$ Using the K_{sp} in **(a)(ii)**, calculate $\Delta G^{\ominus}_{ppt}$ for the precipitation of FeS. Express your answer in kJ mol^{-1}.	**[2]**
			$\Delta G^{\ominus}_{ppt} = 2.303 \times 8.31 \times 298 \times \lg(4.9 \times 10^{-18})$ $= -98719$ J mol^{-1}	

= **<u>– 98.7</u>** kJ mol^{-1} (3 sf)

(iv) Predict how the brown colour intensity of sludge will change when pH decreases. Explain your answer. **[2]**

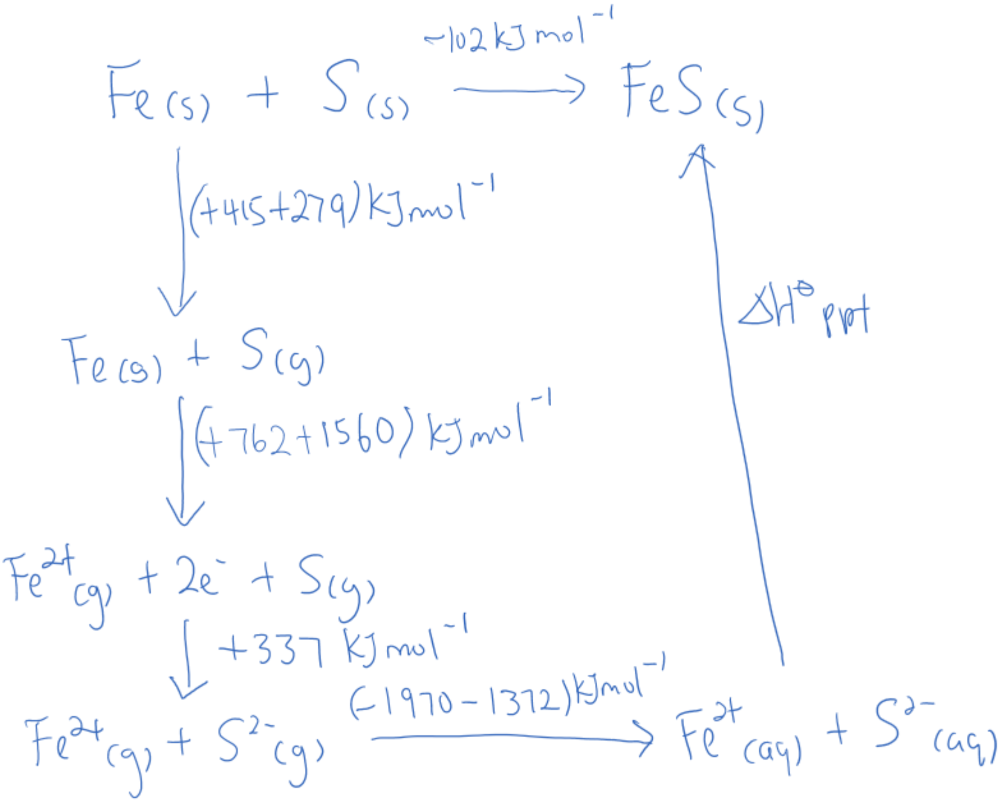
When pH decreases, **<u>$[H^+]$ increases</u>**. By Le Chatelier's Principle, **<u>position of equilibrium 1 will shift left</u>**, **<u>reducing $[S^{2-}]$</u>**. This will in turn cause **<u>position of equilibrium 2 to shift left,</u>** resulting in less FeS solid and hence, the **<u>brown colour intensity will decrease</u>**.

(b) Using data from **Table 2** below, together with relevant data from the *Data Booklet*, draw an energy cycle and calculate $\Delta H^{\ominus}_{ppt}$ for **reaction 2**.

Table 2

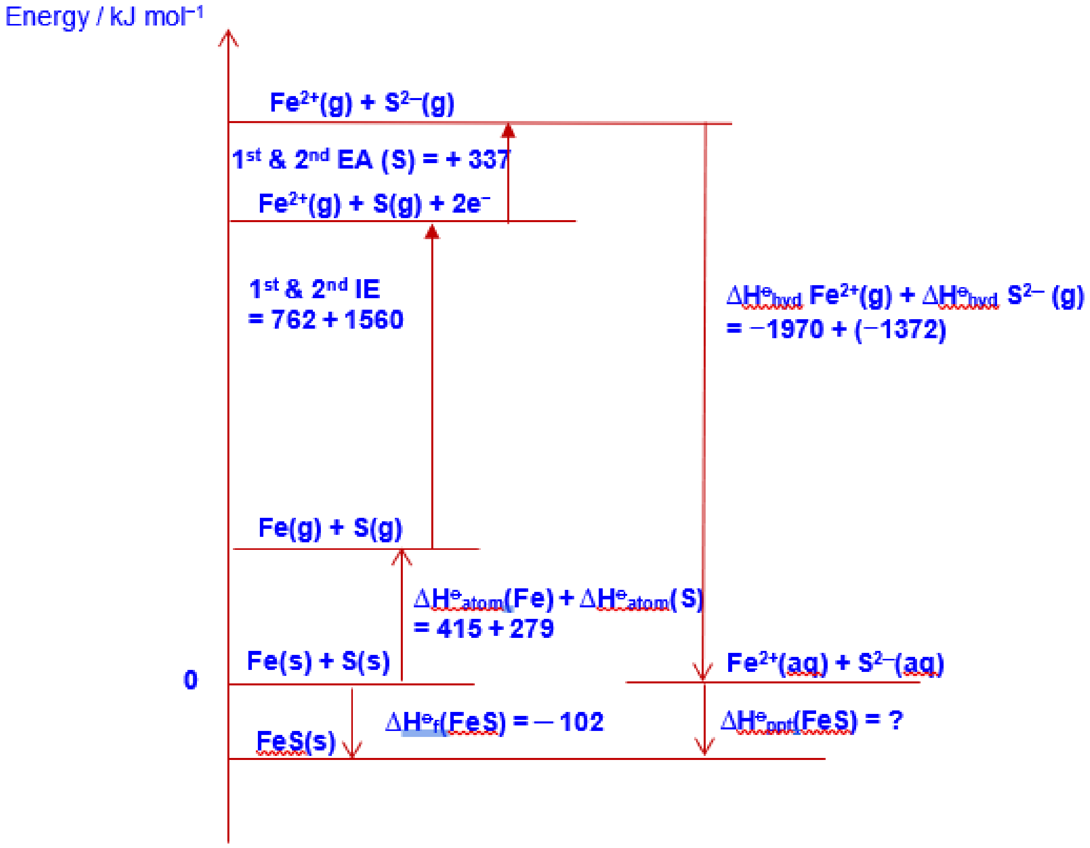
standard enthalpy change of formation of FeS(s)	–102 kJ mol^{-1}
standard enthalpy change of atomisation of Fe(s)	+415 kJ mol^{-1}
standard enthalpy change of atomisation of S(s)	+279 kJ mol^{-1}
sum of first and second electron affinity of sulfur	+337 kJ mol^{-1}
standard enthalpy change of hydration of Fe^{2+}(g)	–1970 kJ mol^{-1}
standard enthalpy change of hydration of S^{2-}(g)	–1372 kJ mol^{-1}

[4]



−102 kJ mol⁻¹
Fe (s) + S (s) → FeS (s)
(+415+279) kJ mol⁻¹
Fe (g) + S (g)
(+762+1560) kJ mol⁻¹
Fe²⁺ (g) + 2e⁻ + S (g)
+337 kJ mol⁻¹
Fe²⁺ (g) + S²⁻ (g)
(−1970 − 1372) kJ mol⁻¹
Fe²⁺ (aq) + S²⁻ (aq)
ΔH° ppt

OR

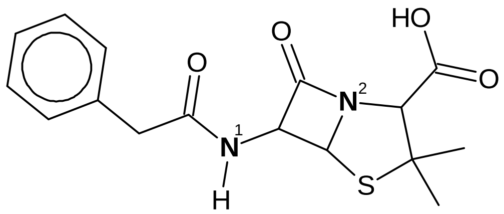


Energy / kJ mol⁻¹
Fe²⁺(g) + S²⁻(g)
1st & 2nd EA (S) = + 337
Fe²⁺(g) + S(g) + 2e⁻
1st & 2nd IE
= 762 + 1560
ΔH°hyd Fe²⁺(g) + ΔH°hyd S²⁻ (g)
= −1970 + (−1372)
Fe(g) + S(g)
ΔH°atom(Fe) + ΔH°atom(S)
= 415 + 279
Fe(s) + S(s)
0
Fe²⁺(aq) + S²⁻(aq)
FeS(s)
ΔH°f(FeS) = − 102
ΔH°ppt(FeS) = ?

		Applying Hess' Law, $-102 = 415 + 279 + 762 + 1560 + 337 - 1970 - 1372 + \Delta H^{\ominus}_{ppt}(FeS)$ $\Delta H^{\ominus}_{ppt}$ (FeS) = **$-$ 113 kJ mol^{-1}** (3 s.f.)		
(c)	**(i)**	Use your answers in **(a)(iii)** and **(b)**, calculate the $\Delta S_{ppt}^{\ominus}$ for the formation of FeS precipitate.		**[1]**
		ecf from (a)(iii) and (b) $\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$ $-98.7 = (-113) - 298\Delta S^{\ominus}$ $\Delta S^{\ominus} = -0.04798$ kJ mol^{-1} K^{-1} $\approx$ **$-$ 0.0480 kJ mol^{-1} K^{-1}** (to 3 sf)		
	(ii)	Hence, explain the significance of the sign of $\Delta S_{ppt}^{\ominus}$ in **(c)(i)**.		**[1]**
		Entropy change is negative because the **degree of disorderliness decreases / less disordered** owing to a **decrease in the number of aqueous particles during precipitation** / aqueous species **are regularly arranged in crystal lattice structure**.		
(d)	Although hydrogen sulfide and water molecules have the same shape, they have slightly different bond angles. State and explain which species has a larger bond angle.			**[2]**
	In H_2O, **oxygen has a greater electronegativity** than sulfur in H_2S. Hence, the **bond pair of electrons are more strongly attracted to oxygen**, resulting in **greater repulsion between the bond pairs** in water. Hence, the **H_2O** has a larger bond angle.			
				[Total: 14]

[TURN OVER

3 Ionisable drugs have acidic, basic or amphoteric properties. An example of an acidic drug is benzylpenicillin G, which is an antibiotic used to treat certain bacterial infection.



benzylpenicillin G

(a) Both nitrogen atoms in benzylpenicillin G are sp^2 hybridised.

(i) Draw the shape of the hybrid orbitals around N^1. **[1]**

(ii) Suggest why sp^2 hybridisation at N^1 and N^2 will make benzylpenicillin G more stable. **[1]**

p orbitals at N^1 and N^2 can overlap sideway with π electron cloud/bond of C=O. Hence, the **lone pair of electrons on N^1 and N^2 can delocalise over N-C-O**. This results in resonance stabilisation.

(iii) Suggest a reason why C─N^2 bond is weaker than C─N^1 bond. **[1]**

There is **ring strain** in the cyclic amide involving N^2. OR
The **bond angle around N^2 (90°) is smaller than the expected (120°)**.

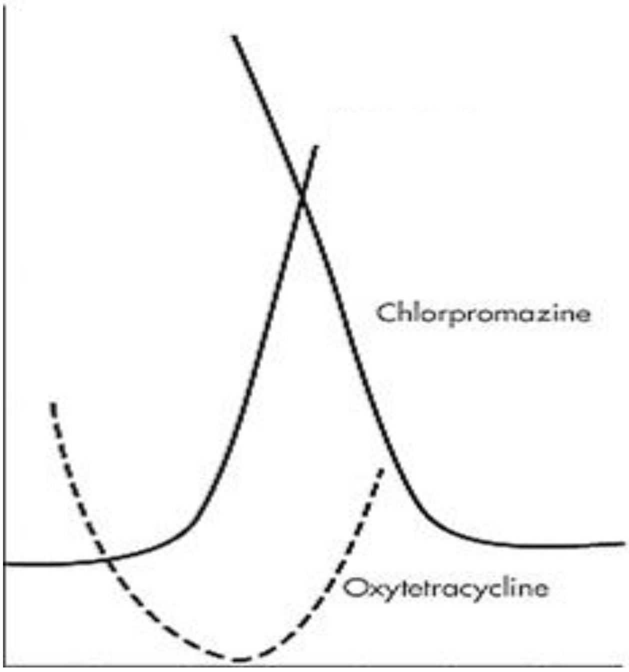
(b) The solubility of three different ionisable drugs is shown in **Fig. 3.1**.

solubility

Benzylpenicillin G

Chlorpromazine

Oxytetracycline

			 **Fig. 3.1**	
		(i)	Explain why the solubility of benzylpenicillin G in aqueous increases from low to high pH.	**[2]**
			At low pH, benzylpenicillin G forms hydrogen bonding with water molecules. At higher pH, the -COOH group of benzylpenicillin G is deprotonated to **-COO$^-$**, which can form **stronger** **ion-dipole interactions with water**. As more energy is released in the formation of ion-dipole interactions with water, benzylpenicillin G is more soluble at higher pH.	
		(ii)	Classify the following compounds according to the type of ionisable drug (acidic, basic and amphoteric).	**[1]**
			Chlorpromazine: **basic** Oxytetracycline: **amphoteric**	
		(iii)	The pH of blood containing benzylpenicillin G is 7.4. Given that the pK_a of benzylpenicillin G is 2.76, calculate the concentration of the undissociated benzylpenicillin G.	**[2]**
			Let benzylpenicillin G be HA. K_a = [H$^+$] [A$^-$] / [HA] $10^{-2.76} = (10^{-7.4})^2$ / [HA]	

			[HA] = **9.12×10^{-13} mol dm^{-3}**	
		(iv)	The Henderson-Hasselbalch equation can be re-expressed to relate the solubility of a drug to the pH of the solution and its pK_a. $pH = pK_a + \log_{10}\left(\frac{S - S_0}{S_0}\right)$ where S is the concentration of the dissolved drug and S_0 is the concentration of the undissociated drug. The solubility of the undissociated benzylpenicillin G in blood with pH 7.4 is 9×10^{-13} mol dm^{-3}. Using the information above and in **(b)(iii)**, calculate the solubility of benzylpenicillin G in blood with pH 7.4. Express your answer in mol dm^{-3}.	**[2]**
			$7.4 = 2.76 + \log\left(\frac{S-9\times10^{-13}}{9\times10^{-13}}\right)$ $10^{4.64} = \frac{S-9\times10^{-13}}{9\times10^{-13}}$ S = 3.928×10^{-8} ≈ **3.93×10^{-8} mol dm^{-3}** (to 3 sf)	
	(c)		Benzylpenicillin G is administered intravenously as potassium benzylpenicillin G, which is an ionic compound. The drug is prepared in a buffer solution made of citric acid, $C_5H_7O_5COOH$ and potassium citrate, $C_5H_7O_5COOK$ to maintain its solubility and stability.	
		(i)	Define the term *buffer.*	**[1]**
			A buffer solution is a solution whose **pH remains almost unchanged** when a **small amount of H$^+$ or OH$^-$ is added to it**.	
		(ii)	Write an equation to show how the citric acid/citrate buffer maintains the pH of the solution when small amounts of alkali are added.	**[1]**
			$C_5H_7O_5COOH + OH^- \rightarrow C_5H_7O_5COO^- + H_2O$	
		(iii)	Explain the difference between the ionic radius and atomic radius of potassium.	**[2]**

			Both K^+ and K have the **<u>same number of protons</u>** and so, **<u>nuclear charge is the same / constant</u>**. K^+ has **<u>one less shell of electrons</u>** than K. Thus, the valence electrons of K experience lower shielding effect. The **<u>valence electrons in K^+ are more strongly attracted</u>** and closer to the **<u>nucleus</u>**. K^+ is **<u>smaller</u>**.	
			[Total: 14]	

4 Compound **X** has the molecular formula $C_8H_8O_2$. It contains 2 different functional groups. Data about the reactions of **X** are given in the table below.

reaction	reagent	observations
1	alkaline aqueous iodine	yellow ppt
2	$Cr_2O_7^{2-}/H^+$, heat	orange solution
3	$Br_2(aq)$	white solid **Y** with M_r = 293.8

(a) **(i)** Based on reaction 1 only, state all the deductions about **X**. **[1]**

X contains a **methyl carbonyl ($CH_3(C=O)$-)** or **methyl alcohol ($CH_3CH(OH)$-)**

(ii) Which deduction in **(a)(i)** is confirmed by reaction 2? Explain your answer. **[2]**

Methyl carbonyl

X **does not get oxidised by $Cr_2O_7^{2-}/H^+$** so it cannot contain a methyl alcohol.

(iii) Based on your answer in **(a)(ii)**, construct an equation to represent reaction 1. You may use R to represent part of compound **X** which does not react with alkaline aqueous iodine. **[1]**

$$\mathbf{R(C{=}O)CH_3 + 3I_2 + 4OH^- \rightarrow RCOO^- + CHI_3 + 3I^- + 3H_2O}$$

(iv) State the type of reaction taking place in reaction 3. **[1]**

Electrophilic substitution

(v) Deduce the molecular formula of **Y**. State the identity of the other functional group found in **X** based on reaction 3. **[3]**

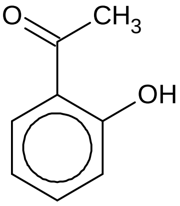
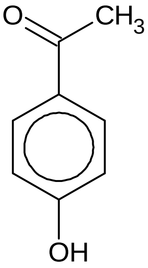
Mr of X = 136.

Increase in Mr of 293.8 – 136 = 157.8 is due to **substitution of 2 H for 2 Br**.

Molecular formula: **$C_8H_6O_2Br_2$**

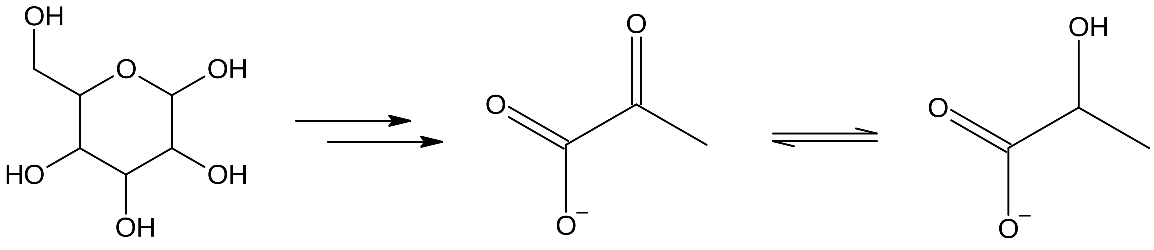
Phenol

(b) Based on your answers in **(a)**, draw the structural formulae of the 2 possible isomers of **X**. **[2]**

		 and 		
			[Total: 10]	

5 Wearables, such as smartwatches and fitness trackers, are gaining popularity with new detecting abilities constantly being developed.

In recent years, research has been done to integrate chemical sensors into wearables to detect metabolites in sweat. One such metabolite is lactate, which can be used to determine the fatigue level of muscles in our body. Under conditions of high energy demand, glucose breaks down rapidly into lactate, which accumulates in the muscles. **Fig. 5.1** shows the breakdown of glucose to pyruvate, and eventually to lactate (M_r = 89.0).



glucose pyruvate lactate

Fig. 5.1

Table 5.1 shows the lactate concentration in sweat before and after intense exercise.

Table 5.1

	Lactate concentration (mol dm^{-3})	
	before exercise	after exercise
sweat	2.0×10^{-4}	6.2×10^{-4}

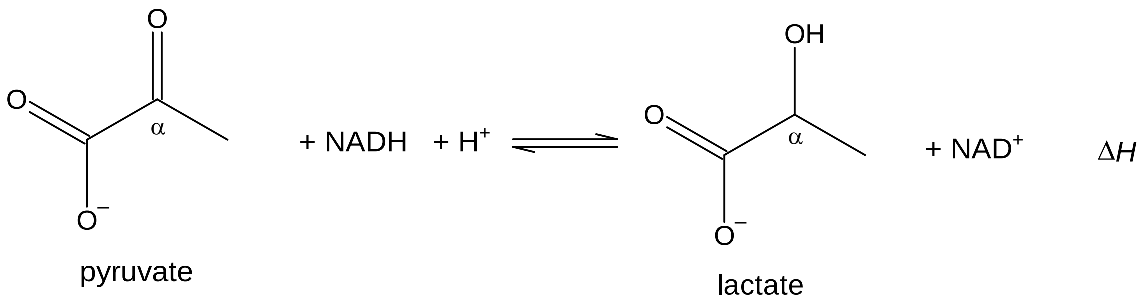
Table 5.2 shows the possible lactate concentration ranges that can exist in blood.

Table 5.2

Lactate concentration (mmol dm^{-3})	Medical condition
0.5 - 1	Normal
2 - 4	Hyperlactatemia
> 4	Acidosis

(a) **(i)** State the number of chiral centres present in glucose molecule. **[1]**

5

		(ii)	A normal person loses an average of $3.5\ \text{dm}^3$ of sweat for every hour of exercise. Using the data in **Table 5.1**, calculate the mass of lactate lost in sweat after two hours of intense exercise.	**[2]**
			Volume of sweat lost = $3.5 \times 2 = 7\ \text{dm}^3$ Amount of lactate lost = $7 \times [(6.2 \times 10^{-4}) - (2.0 \times 10^{-4})] = 0.00294$ mol Mass of lactate lost = $0.00294 \times 89.0 = 0.2616 \approx$ **0.262 g** (to 3 sf)	
		(iii)	$10\ \text{cm}^3$ of blood was drawn from an individual and the mass of lactate was found to be 0.0027 g. Determine the medical condition of this individual.	**[1]**
			[lactate] = [(0.0027 / 89)] / 0.01 = **0.003033** mol dm^{-3} = 3.03 mmol dm^{-3} The individual suffers from **hyperlactatemia**.	
	The reduction of pyruvate to lactate involves a compound known as reduced nicotinamide adenine dinucleotide (NADH). The reduction is an equilibrium where all species are in aqueous state.  K_c value for this equilibrium at 298 K is 1.46×10^{11}.			
	(b)	**(i)**	State the change in oxidation number for carbon α.	**[1]**
			+2 to 0 OR Change is **-2**	
		(ii)	During an intense exercise, the pH of blood decreases from 7.4 to 7.1. Assuming that [NADH] is equal to [NAD^+], calculate the [lactate] / [pyruvate] ratio at pH 7.1.	**[2]**
			$1.46 \times 10^{11} = \frac{[\text{lactate}]}{[\text{pyruvate}][10^{-7.1}]}$ $\frac{[\text{lactate}]}{[\text{pyruvate}]} = 11597 \approx$ **11600** (to 3 sf)	

(iii) **Fig. 5.2** shows the graph of [lactate] / [pyruvate] against time. At time t_1, the temperature of the reaction was increased.

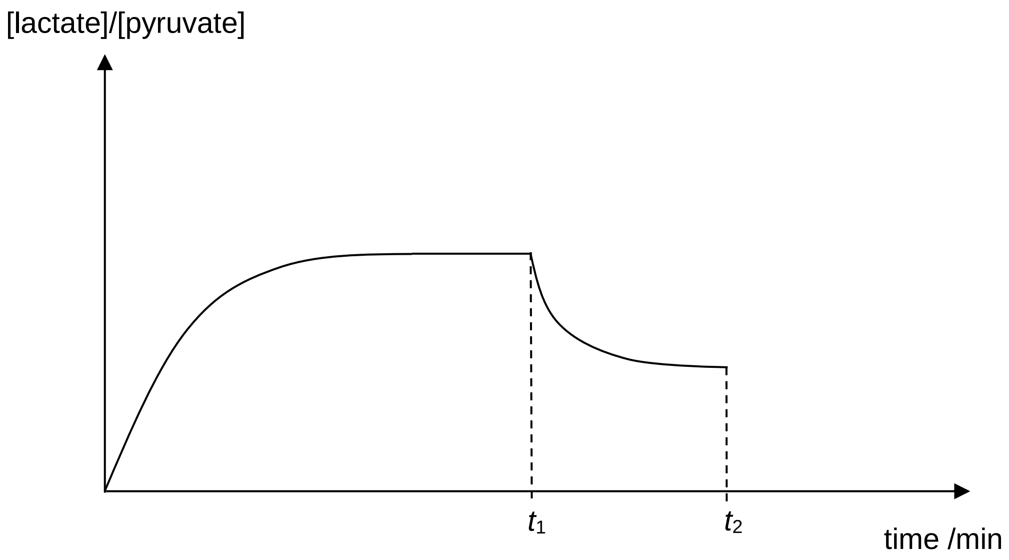


Fig. 5.2

Determine the sign of ΔH for this reaction. Explain your answer. **[2]**

At time t_1, when temperature is increased, **ratio decreased**. Hence, the **position of equilibrium has shifted left** to **absorb the excess heat**. This meant that the **favoured** **backward reaction is endothermic**, the forward reaction is exothermic, **ΔH is negative**.

(iv) On **Fig. 5.2**, complete the diagram to show the effect on [lactate] / [pyruvate] when OH^- was added to the reaction mixture at time t_2. **[1]**

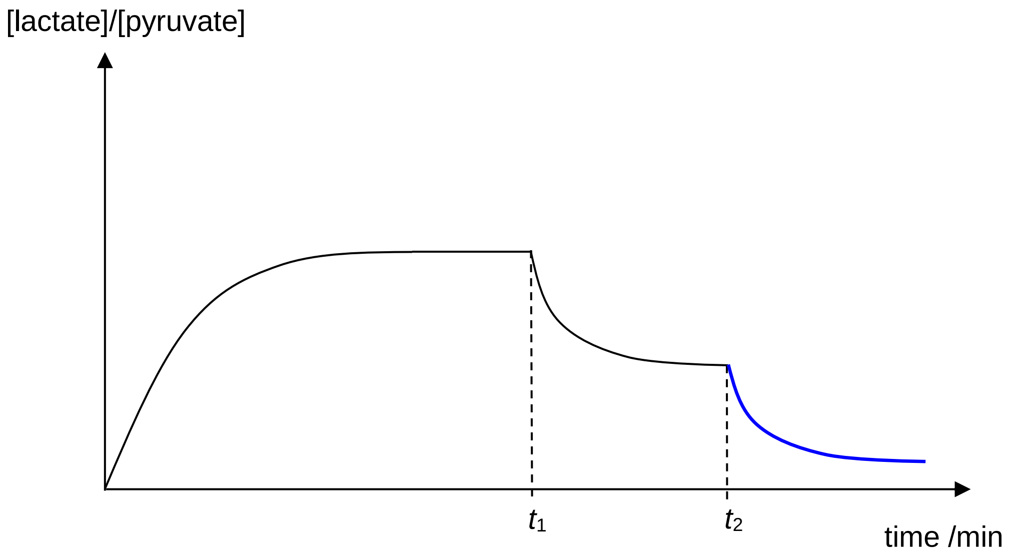


Fig. 5.3 shows the reduction of pyruvate. This reaction happens in the following manner.

- The lone pair of electrons on N of NADH delocalises into a nearby alkene. This causes the π bond to be broken but a new one is subsequently formed.
- A C─H bond of NADH breaks and the two electrons form a σ bond with carbonyl carbon of pyruvate.
- The π bond of C=O breaks and a σ bond is formed with H^+ as shown.

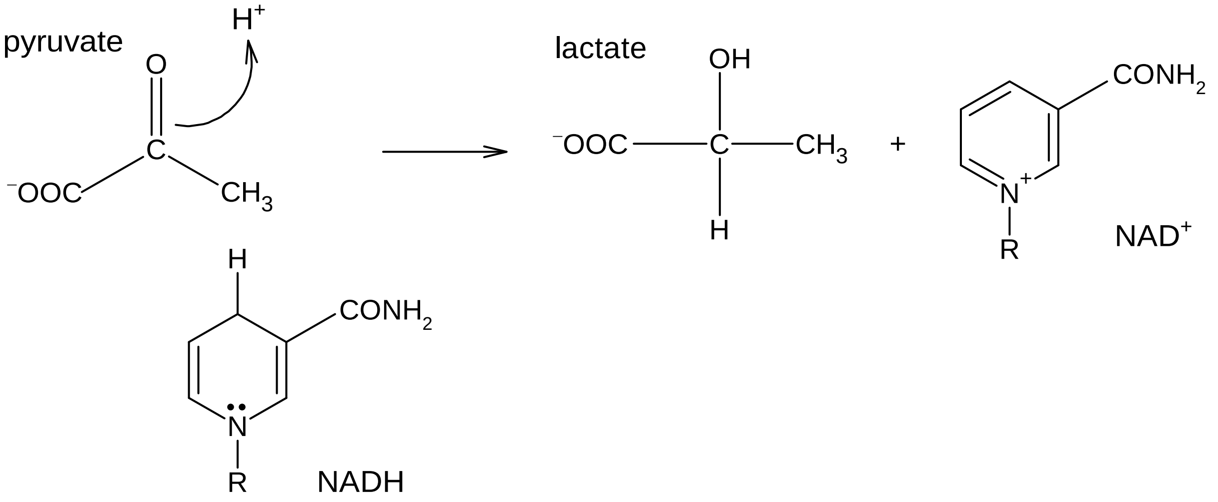
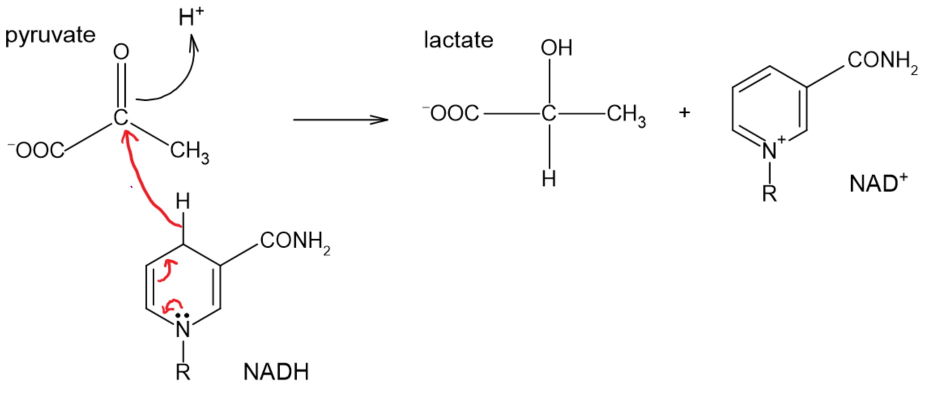
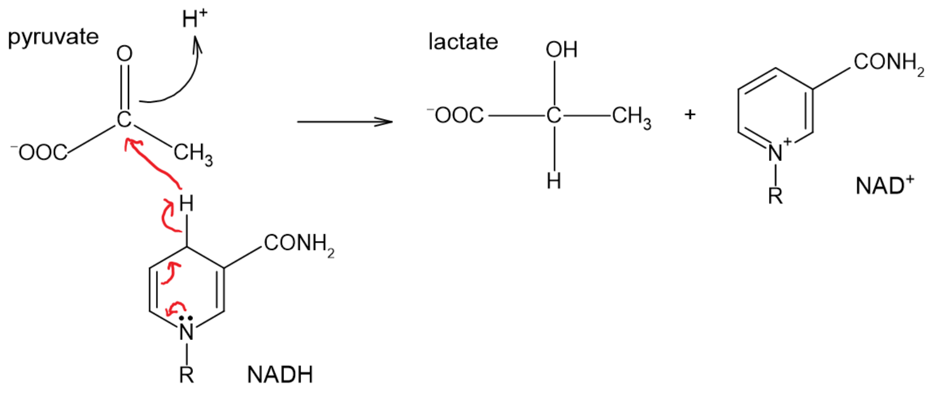


Fig. 5.3

(v) On **Fig. 5.3**, draw curly arrows to show the movement of electron pairs when NADH reduces pyruvate into lactate. **[2]**



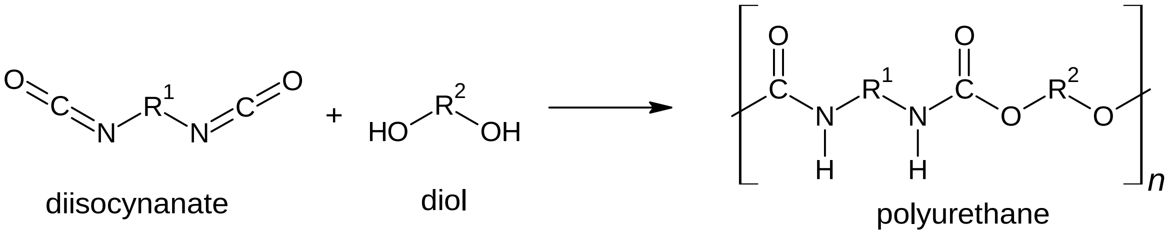
OR



(c) Polyurethane is a polymer used to make the straps of fitness bands and smartwatches as they have good resistance towards salt water and ultra-violet radiation. Hence, unlike cheaper plastic or resin straps, polyurethane straps are more suited for a wide range of sporting activities.

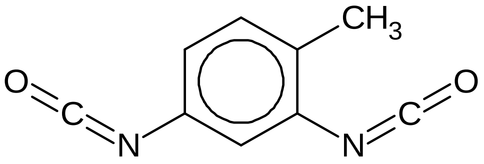
The reaction between diisocyanate and diol to form polyurethane is shown in **Equation 1**.

Equation 1



n = degree of polymerisation

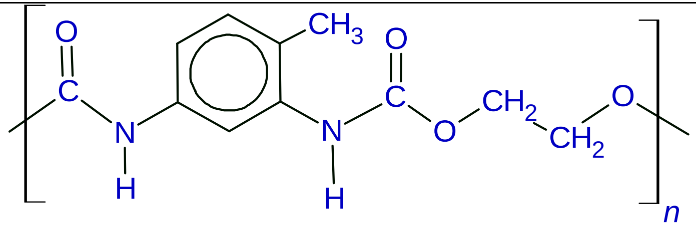
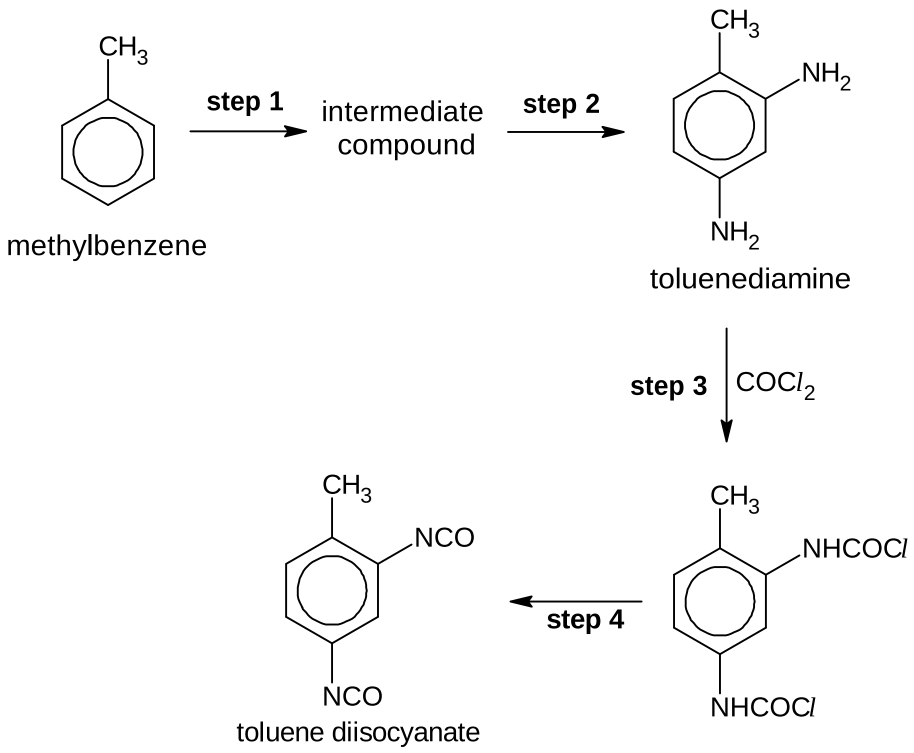
(i)



toluene diisocyanate (M_r: 174)

Suggest the structure of the polyurethane polymer formed when toluene diisocyanate is reacted with ethane-1,2-diol.

[1]

				
		(ii)	The average molar mass of the polyurethane polymer formed in **(c)(i)** is 1.3688×10^4 g mol^{-1}. Calculate the degree of polymerisation, *n*, for this polymer.	**[1]**
			n = 13688 / (174 + 12.0 x 2 + 6 x 1.0 + 16.0 x 2) = **58** *ecf from (c)(i)*	
	(d)	Toluene diisocyanate is synthesised from methylbenzene by the following route. 		
		(i)	Complete the reaction scheme to show how toluenediamine could be synthesised from methylbenzene in two steps. Show the structure of the intermediate product and state the reagents and conditions for each step.	**[3]**
			Step 1 …………………………………………………………………………… **Step 2** ……………………………………………………………………………	

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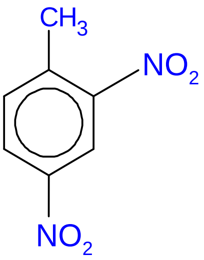
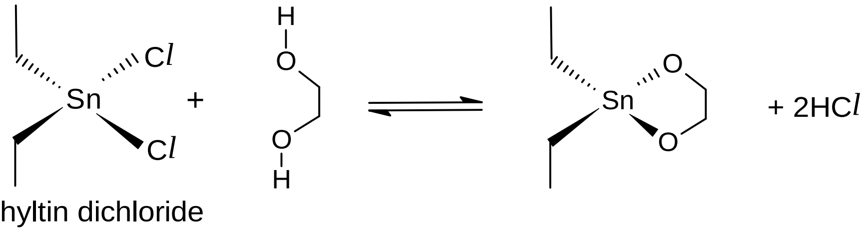
			intermediate compound	
			step 1: conc H_2SO_4, conc HNO_3 step 2: Sn, conc HC*l* heat, followed by (excess) NaOH (aq) 	
		(ii)	Suggest the type of reaction in **step 4**.	**[1]**
			Elimination	
		(iii)	The reaction between toluenediamine and phosgene gas, $COCl_2$, in **step 3** is carried out at a temperature of 500 °C and 400 kPa. Assuming the process is 100% efficient, calculate the volume of phosgene required to produce 1 kg of toluene diisocyanate.	**[2]**
			Amount of phosgene required = (1000 / 174) x 2 = 11.494 mol (400 x 1000) V = 11.494 x 8.31 x (500 + 273) V = 0.1845 m^3 ≈ **0.185 m^3** (to 3 sf)	
		(iv)	Phosgene gas is known to exhibit non-ideal gas behaviour. State a reason for this observation.	**[1]**
			There are **significant permanent dipole-permanent dipole interactions between phosgene molecules**. OR	

			The **volume / molecular size of each phosgene molecule is significant compared to the total volume occupied by phosgene gas sample**.	
		(v)	Toluene diisocyanate must be stored in an anhydrous condition. In the presence of water, toluene diisocyanate will react to form toluenediamine and an acidic gas. Suggest the identity of the acidic gas.	**[1]**
			CO_2	
	(e)	The production of polyurethane occurs in the presence of diethyltin dichloride catalyst. Tin atoms are capable of undergoing ligand exchange with ethane-1,2-diol as shown in **Fig. 5.4**.  **Fig. 5.4**		
		(i)	Suggest how the presence of a catalyst would affect the magnitudes of the rate constant, k, and activation energy, E_a, of the reaction in **Fig. 5.4**.	**[1]**
			The presence of a catalyst will **increase rate constant** and **decrease activation energy**.	
		(ii)	Suggest a chemical test to show that ligand exchange has occurred according to **Fig. 5.4**. Include the expected observations in your answers.	**[2]**
			Add **$AgNO_3$(aq)** followed by NH_3 (aq). **White ppt observed**, soluble in NH_3(aq) to form colourless solution. OR Add **Na_2CO_3(aq)**. **Effervescence observed. Gas formed white ppt in aq $Ca(OH)_2$**.	
				[Total: 25]