2018 Y6 H2 Chemistry Preliminary Exams Paper 2 (Suggested Solutions)

1(a) X is likely to be in <u>Group 14</u> as there is a <u>large jump from the 4th to 5th</u> ionisation energies. This shows that the <u>5th electron is removed from an inner electron shell</u> and requires more energy for removal as it is more strongly attracted to the nucleus. Hence, there are 4 valence electrons in X.

Since **X** has at least 10 electrons but fewer than 20 electrons, <u>**X** is Si</u>.

<u>Comments</u>

- Students need to be familiar with the Group number in the Periodic Table given in the Data Booklet. Silicon is a Group 14 (NOT Group 4 or Group IV) element.
- Since X has at least 10 electrons, carbon is not a possible answer for X.
- Answers need to be specific when referring to the <u>5th</u> electron being removed from the <u>inner</u> electron shell. Avoid using vague phrases like 'different electron shell' or 'another electron shell'.
- 1(b) Mn and Fe are first-row transition metals. Although Fe has a <u>higher nuclear charge</u> (greater proton number) than Mn, Fe has <u>more 3d electrons which provide more shielding</u> between the nucleus and the outer 4s shell of electrons. This <u>increase in shielding effect offsets the increase in nuclear charge</u> and hence, the increase in effective nuclear charge from Mn to Fe is minimal, resulting in the first ionisation energies of Mn and Fe to be similar.

Comments

- Most students were able to identify that Fe has both higher nuclear charge and shielding effect than Mn. However, students need to be clearer in their explanation on why the increase in effective nuclear charge from Mn to Fe is minimal.
- **1(c)** Ca²⁺ has a <u>larger cationic radius</u> than Cu²⁺, thus Ca²⁺ has a <u>lower charge density and weaker</u> polarising power.

Consequently, there is lower extent of distortion of the electron cloud of the carbonate anion and hence <u>covalent bonds within the carbonate anion are weakened to a lesser extent</u>. Hence, <u>CaCO₃ decomposes at a higher temperature</u>.

Comments

- Most students were able to link the larger cationic radius of Ca²⁺ to its lower charge density and weaker polarising power.
- Students are required to make the link between the stronger covalent bonds within the carbonate anion of CaCO₃ to its higher decomposition temperature.
- **2(a)(i)** Anthracene is a cyclic molecule. All carbon atoms of anthracene are <u>sp² hybridised</u> and are trigonal <u>planar</u>.

The unhybridised p-orbitals of the carbon atoms in anthracene can form a continuous <u>p-orbital overlap</u>, thus the π <u>electrons are delocalised</u> throughout the molecule.

Anthracene has $4(3) + 2 = \underline{14} \pi \underline{\text{electrons}}$ where or $\underline{n = 3}$.



Comments

- Most students correctly identified the hybridisation of the carbon atoms as sp² and also stated that the unhybridised p-orbital of the carbon atoms form a continuous overlap allowing the electrons in the p-orbitals to be delocalised forming the π-electron cloud.
- Most students also correctly calculated the number of π -electrons or the value of n.
- Answers which simply restated the bulleted points, i.e. criteria for aromaticity (e.g. the π-electrons are delocalised throughout the molecule), without stating that this is possible through the continuous p-orbital overlap were not given any credit.

2(a)(ii) Enthalpy change of hydrogenation = $7(-118) = -826 \text{ kJ mol}^{-1}$

Comments

Most students correctly calculated this value.





Enthalpy change of hydrogenation = $-356 - 129 = -485 \text{ kJmol}^{-1}$

- Most students correctly calculated the enthalpy change of hydrogenation.
- For the energy level diagram, some incorrect or missing state symbols were commonly observed, particularly for anthracene and tetradodecahydroanthracene.
- Incorrect coefficient for H₂(g) was also commonly observed.
- Some students missed out the arrow for ΔH_2 .

2(a)(iv) Resonance energy = $826 - 485 = 341 \text{ kJ mol}^{-1}$

(energy level diagram – not required by question)



Comments

Most students correctly calculated the value of the resonance energy.

2(b)(i) $TEQ = (0.029 \times 0.01) + (0.135 \times 0.01) + (0.204 \times 1.00) = 0.20564 = 0.206$

Comments

Most students correctly calculated the value of the TEQ.

ECR = $\frac{0.20564}{70}$ x 1.37 x 10⁻³ = $\frac{4.00 \times 10^{-6}}{100}$ 2(b)(ii)

> Since the ECR from the consumption of smoked fish exceeds the value set by USEPA, it will be a <u>cancer risk</u> for the 70 kg person.

Comments

- Most students correctly calculated the value of the ECR and came to the correct conclusion.
- Based on the question, answers need to conclude if there will be a cancer risk.

2(c)(i)



Comments

- Generally well done.
- Answers need to show the correct positions of the methyl and isopropyl (-CH(CH₃)₂) groups on thymolphthalein.
- The phenol -OH group is a 2,4-directing group. Hence students should not give the minor product where the substitution occurred at position 3 with respect to the phenol group of thymol.
- 2(c)(ii) <u>Thymol reacts more readily</u> as the <u>alkyl groups of thymol are electron donating and increase</u> <u>the electron density on the benzene ring</u> making it more susceptible to electrophilic substitution.

Comments

- This part was very well done by most students.
- Answers which concluded that phenols react more readily as there is <u>less steric hindrance due to</u> <u>absence of alkyl groups</u> were accepted for this question.
- It is incorrect to state that the alkyl groups increased the intensity of *negative charge* on thymol as the thymol molecule has no charges.
- Students need to avoid contradiction in their answers.
- 2(d) The carboxylate anion in **A** is more stable than the phenoxide anion in **B** as the <u>negative</u> <u>charge on oxygen is dispersed over the two highly electronegative oxygen atoms</u> resulting in two equivalent resonance structures in **A** as compared to **B**.

Comments

- This part was very well done by most students.
- It is incorrect to mention steric hindrance/strain in **B** as the single bonds connecting the phenol rings to phthalic anhydride can rotate to minimise steric hindrance.
- In general, 5-membered and 6-membered rings are stable. Hence answers should not discuss about ring strain in the 5-membered ring in **B**.
- 3(a)(i) The stronger the base, the more available is its lone pair of electrons for donation to acid. Hence, <u>a strong Lewis base will readily donate its lone pair to the electron deficient carboxyl</u> <u>C (Lewis acid) to reform the starting acid derivative</u>. Thus, strong Lewis bases are poor leaving groups.

or

Strong Lewis bases donate electron pair more easily and are less likely to accept an electron pair. Thus, it is more difficult to break the C-Y bond to form Y^- .

<u>Comments</u>

- Many students concluded that strong Lewis bases are poor leaving groups as they form stronger bonds with the carbonyl carbon. This may not be correct as C-N bond is weaker than C-O bond but NH₂⁻ is a stronger base than OH⁻.
- There are also students who suggested that strong Lewis bases repel the bond pair of electrons in the C-Y bond. This is incorrect because when Y is covalently bonded to C, it is not a Lewis base. Only when the C-Y bond breaks and Y leaves as :Y⁻, then Y⁻ is considered a Lewis base as it has an electron-pair that can be donated.

3(a)(ii) Since pK_b of CH_3COO^- is more positive than NH_2^- , CH_3COO^- is a weaker base and is hence a better leaving group so that the reactivity of $(CH_3CO)_2O$ is higher than that of CH_3CONH_2 . Reaction **1** will proceed with a faster rate than reaction **2**.

or

The p K_b of CH₃O⁻ is less positive than that of CH₃COO⁻ but more positive than that of NH₂⁻. Hence the product CH₃COOCH₃ is less reactive than (CH₃CO)₂O but more reactive than CH₃CONH₂. Thus, reaction **1** is likely to have a higher yield, as the product is less reactive than the reactant so that the backward reaction is less likely to occur, resulting in higher yield.

Comments

- This part was generally well done by most students.
- Students should describe the <u>pKb</u> of the <u>leaving group Y⁻</u>(CH₃COO⁻/NH₂⁻/CH₃O⁻) instead of ethanoic anhydride/ethanamide/ester/methyl ethanoate.
 They should then conclude on the <u>relative reactivity</u> of the <u>ethanoic anhydride/ethanamide/ester/</u>

methyl ethanoate and the relative yield/rate of reaction 1 versus reaction 2.

 Some students incorrectly suggested that Y⁻ is a conjugate base. Note that a conjugate acid-base pair differs only by one H⁺.

3(b)(i) Initial amount of
$$CH_3OH = \frac{20 \times 0.792}{32.0} = 0.495 \text{ mol}$$

Comments

• This part was well done.

3(b)(ii) $n_{CH3COOH}$ in 5.00 cm³ of eqm mixture = $n_{NaOH} = \frac{16.80}{1000} \times 0.500 = 0.00840$ mol

 $n_{CH3COOH}$ in 40.00 cm³ of eqm mixture = 0.0084 x $\frac{40.00}{5.00} = 0.0672$ mol

Comments

- This part was relatively well done.
- A small number of students thought that NaOH reacts with the ester rather than with CH₃COOH. Students should note that hydrolysis of ester by base or acid requires heating. Hence the OH⁻ used in the titration does not react with the ester but only reacts with CH₃COOH.

3(b)(iii) $K_c = \frac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$

- Many students omitted water from the expression. Students should take note that pure alcohol and acid are used, as indicated by the state symbol (I) in the equation. H₂O formed is present in a small amount only as aqueous solutions of the alcohol and acid are not used. Thus, [H₂O] is not a constant but varies with the reaction.
- [H₂O] is left out of the K_c expression only if [H₂O] is a constant, e.g. when H₂O is present as a solvent.

3(b)(iv) $n_{CH3COOH}$ reacted = 0.350 - 0.0672 = 0.2828 mol

	CH ₃ OH(I) +	- CH ₃ COOH(I)	\Rightarrow CH ₃ COOCH ₃ (l) + H ₂ O(l)
Initial amt/ mol	0.495	0.350	0	0
Change in amt/ mol	-0.2828	-0.2828	+0.2828	+0.2828
Final amt/ mol	0.2122	0.0672	0.2828	0.2828
$\mathcal{K}_{c} = \frac{(\frac{0.2828}{V})(\frac{0.2828}{V})}{(\frac{0.2122}{V})(\frac{0.0672}{V})} + \frac{1}{2}$	= <u>5.61</u>			

Comments

- Students should take note that concentration (rather than amount) is substituted into the K_c expression to determine the value of K_c . For this particular reaction, the volume terms cancel out so that the answer obtained for $\frac{[CH_3COOCH_3][H_2O]}{[CH_3COOH][CH_3OH]}$ is the same as $\frac{n_{CH_3COOCH_3 \times n_{H_2O}}}{n_{CH_3COOH \times n_{CH_3OH}}}$. For reactions where the volume terms do not cancel out, students are reminded to convert amount to concentration to determine the value of K_c .
- Some students used the initial amount of CH₃OH and CH₃COOH instead of the equilibrium amount for determining K_c.
- Some students used the incorrect change in amount i.e. 0.0672 instead of 0.2828.
- **3(b)(v)** The mixture was added to a large amount of ice-cold water to quench it. <u>Cooling and diluting</u> the reaction mixture slows down the reaction so that the equilibrium position would not shift during the titration and the equilibrium concentration of CH₃COOH can be determined.

Comments

- This part was generally well done.
- **3(c)** <u>Warm</u> the esters separately with <u>aqueous alkaline iodine</u>. The ester that gives a <u>yellow precipitate</u> of CHI₃ is <u>HCOOCH₂CH₃</u>. No yellow precipitate for CH₃COOCH₃.

 $\begin{array}{l} \mathsf{HCOOCH}_2\mathsf{CH}_3 + \mathsf{OH}^- \longrightarrow \mathsf{HCOO}^- + \mathsf{CH}_3\mathsf{CH}_2\mathsf{OH} \\ \mathsf{CH}_3\mathsf{CH}_2\mathsf{OH} + 4\mathsf{I}_2 + 6\mathsf{OH}^- \longrightarrow \mathsf{HCOO}^- + \mathsf{CHI}_3 + 5\mathsf{I}^- + 5\mathsf{H}_2\mathsf{O} \\ [\mathsf{or} \quad \mathsf{HCOOCH}_2\mathsf{CH}_3 + 4\mathsf{I}_2 + 7\mathsf{OH}^- \longrightarrow 2\mathsf{HCOO}^- + \mathsf{CHI}_3 + 5\mathsf{I}^- + 5\mathsf{H}_2\mathsf{O}] \end{array}$

Comments

Many students incorrectly concluded that methyl ethanoate, CH₃COOCH₃, gave yellow ppt (CHI₃) for the iodoform test. Students should note that compounds which give a positive iodoform test must have the following structures (refer to Carbonyl Compound Lecture notes, pg 18):





 Students should note that there is no direct identification test for an ester. The ester needs to be hydrolysed first and identified by the carboxylic acid or alcohol formed.

Hence, to distinguish between methyl ethanoate or ethyl methanoate, first consider the products formed when these esters are hydrolysed:

Methyl ethanoate: $CH_3COOCH_3 + H_2O \longrightarrow CH_3COOH + CH_3OH \qquad \cdots$ Ethyl methanoate: $HCOOCH_2CH_3 + H_2O \longrightarrow HCOOH + CH_3CH_2OH \cdots$

Of the products, only CH_3CH_2OH formed in O gives a positive CHI_3 test and hence the two esters may be distinguished by warming the esters separately with aqueous alkaline iodine. It is not necessary to warm the esters with dilute acid first because aq NaOH used in the CHI_3 test causes the ester to undergo base hydrolysis when warmed.

As HCOOH formed in @ contains the H–C=O structure, ethyl methanoate gives a positive test when warmed with Tollens' reagent or Fehling's solution, giving a silver mirror or brick red ppt of Cu₂O respectively. Since both reagents contain OH⁻ ions, ethyl methanoate undergoes base hydrolysis, forming HCOO⁻ which then reacts with the reagents as shown below:

Tollens' reagent: $HCOO^- + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CO_3^{2^-} + 2Ag + 4NH_3 + 2H_2O$ Fehling's solution: $HCOO^- + 2Cu^{2^+} + 5OH^- \longrightarrow CO_3^{2^-} + Cu_2O + 3H_2O$

- The esters cannot be distinguished by warming with acidified aq KMnO₄ or K₂Cr₂O₇. Both esters hydrolyse to form products which can be oxidised by KMnO₄ or K₂Cr₂O₇. CH₃OH from ① is oxidised to CO₂ while HCOOH and CH₃CH₂OH from ② are oxidised to CO₂ and CH₃COOH respectively.
- **3(d)** Add <u>dilute hydrochloric acid to the mixture</u>. <u>Stir</u> and <u>filter</u> the mixture. **Q** is obtained as a salt in the filtrate while **P** is obtained as the residue.

Q is an amine and is basic. **Q** reacts with the acid to produce $(C_6H_5)_2NH_2^+$ (or salt) which forms strong ion–dipole interactions with water, resulting in its dissolution. Thus, **Q** dissolves in dilute hydrochloric acid and can be separated from **P** by filtration.

- This question was poorly done.
- An organic compound with 6 carbons or more and with very few functional groups which can form hydrogen bond with H₂O is likely to be insoluble in water, unless it has a charge. Thus, one way to separate amide P from amine Q is to convert the amine Q to a salt by reacting the mixture with a dilute acid followed by filtration.
- Hydrolysis by warming the mixture with dilute acid or base is not accepted as an answer. This is because the hydrolysis of P causes P to break down to C₆H₅COOH and CH₃NH₃⁺ (acid hydrolysis) or C₆H₅COO⁻ and CH₃NH₂ (base hydrolysis). P should be kept intact after separation from Q.
- The following reagents are ineffective in separating **P** from **Q**:
 - Concentrated acid \Rightarrow insufficient water to dissolve **Q**
 - Aq Br₂ \Rightarrow even though **Q** reacts with aq Br₂, the product cannot be separated from **P** as both are insoluble.
 - 2,4–DNPH ⇒ both **P** and **Q** do not react with 2,4–DNPH. Even though **P** contains the –C=O group, it is an amide and not a carbonyl compound. Hence, it does not react with 2,4–DNPH.
 - Aq NaOH (or other bases) \Rightarrow amine **Q** does not react with a base. Amide **P** does not react with a base unless heat is applied.

4(a)(i) It is the <u>energy change</u> when <u>one mole</u> of the substance is <u>completely dissolved</u> in a solvent to form an <u>infinitely dilute</u> solution at <u>298 K and 1 bar</u>.

Comments

- Students need to take note that the enthalpy change of solution can either be exothermic or endothermic. Hence, it is more appropriate to use energy "change" in the definition. Energy "absorbed", "required", "used" or "released" will not be accepted.
- Standard conditions (298 K, 1 bar) were frequently confused with standard temperature and pressure (s.t.p.) for gases (273 K, 1 bar).
- Some students showed confusion between standard enthalpy change of solution and standard enthalpy change of hydration. Standard enthalpy change of hydration (ΔH_{hyd}^{\ominus}) of an ion is the <u>energy</u> released when <u>one mole</u> of the gaseous ion is hydrated at <u>298 K and 1 bar</u>.

4(a)(ii) $\Delta T = 37.0 - 25.0 = +12.0 \text{ °C}$



Comments

- Most students confused this graph with the inverted V-shaped graph from a thermometric titration.
- The graph shows the temperature against time. An extrapolation of the graph (before the addition of the solid and the "cooling curve") to the time of addition of the solid (i.e. at t = 75 s) should be done in order to obtain the temperature change for the reaction.

4(a)(iii) Heat absorbed by water = mc∆T = 100 x 4.18 x (12.0) = 5016 J Mr of anhydrous MgSO₄ = 24.3 + 32.1 + 4(16.0) = 120.4 Amt of anhydrous MgSO₄ used = (7.500 / 120.4) = 0.06229 mol $\Delta H_{sol}^{\ominus} = -(5016 / 0.06229) = -80527 \text{ J mol}^{-1} = -80.5 \text{ kJ mol}^{-1}$

<u>Comments</u>

- Generally well done based on the value of △*T* in 4(a)(ii).
- Some students left out the negative sign for ΔH_{sol}^{\ominus} as they forgot that a temperature rise means heat was given out by the reaction (i.e. reaction is exothermic).

<u>The heat capacity of cup/calorimeter was not taken into consideration.</u> Account for the heat capacity of the cup/calorimeter by <u>calibrating the calorimeter using a sample with known</u> ΔH_{soln} .

or

The solution formed was not sufficiently dilute. Use a larger volume of water or use less solid.

Comments

- This question was very poorly answered. Many students wrote "heat lost to the surroundings" without realising that this was accounted for by the extrapolation of the "cooling curve" in **(a)(ii)**.
- A number of students attributed the different values to the evaporation of solution, which is not significant enough to account for the difference in values.

4(a)(v) $\Delta H_r^{\ominus} = -88.0 - (+16.0) = -104 \text{ kJ mol}^{-1}$

Comments

• Generally well done.

 Some students did not read the question carefully. The question requires the use of ∆H_{sol}[⊕] = − 88 kJ mol⁻¹ from (a)(iv), and not their calculated value in (a)(iii).

4(b)

Energy / kJ mol⁻¹



 $-1278 = +148 + 736 + 1450 + \Delta H_{f}^{\ominus}(SO_{4}^{2-}(g)) - 2705 \Delta H_{f}^{\ominus}(SO_{4}^{2-}(g)) = -907 \text{ kJ mol}^{-1}$

Comments

- This is generally well done, although a handful of students gave an energy cycle instead of an energy level diagram.
- Do note that <u>state symbols are compulsory</u> for energy level diagrams. The same applies for energy cycles.
- Students are reminded of the need for clear handwriting. For instance, the state symbols "s" and "g" need to be written clearly.
- There is no need to use BE(O=O) because the question only requires you to determine $\Delta H_f(SO_4^{2-})$.
- The ionisation of Mg (to form Mg²⁺ and 2e⁻) should come <u>before</u> ΔH_f (SO₄²⁻) as the latter process requires electrons from the ionisation of Mg.
- Many students missed writing the 2 moles of electrons for the ionisation of Mg. Do note that it is important to <u>balance mass (i.e. atoms) and charges</u> for every step in the energy level diagram.





Comments

• $\operatorname{Cu}^{2+} + 2e^{-} \rightleftharpoons \underline{\operatorname{Cu}} \quad E^{\ominus} = +0.34 \text{ V}$

Ag⁺ + e⁻ \rightleftharpoons <u>Ag</u> E^{\ominus} = +0.80 V (more positive, hence greater tendency to undergo reduction \Rightarrow cathode)

Choosing the electrodes: The metals themselves are components of the half-reactions and should be used as the electrodes. Some students used Pt as electrodes. That should only be the case when none of the species in the half reaction can be used as the electrode.

Electrolyte ions: The electrolyte should be 1 mol dm⁻³ Cu²⁺ (aq) for the anode and 1 mol dm⁻³ Ag⁺ (aq) for the cathode. Do not introduce other ions like H⁺ since it is not a component of the half-cell. *Flow of electrons*: Electrodes flow from anode (loss of electrons) to cathode (gain of electrons) in an electrochemical cell. Please label the electrons with 'e^{-'}.

Do not confuse standard conditions with standard temperature pressure (s.t.p). The standard conditions for electrochemical cells and enthalpy changes are 298 K (25°C) and 1 bar while s.t.p. (found in the Data Booklet) is 273 K (0°C) and 1 bar (10⁵ Pa).

5(a)(ii)
$$E^{\ominus}_{cell} = E^{\ominus}_{cathode} - E^{\ominus}_{anode}$$

= +0.80 - (+0.34)
= +0.46 V

- Generally well done except for careless mistakes in calculations, forgetting the '+' sign, or not giving the units.
- Few students made the error of using $E^{\ominus}_{anode} = +0.15$ V, which is the reduction potential for Cu⁺ to Cu.

5(a)(iii) Upon addition of NH₃, <u>blue ppt forms</u>. $Cu^{2+}(aq) + 2OH^{-}(aq) \rightleftharpoons Cu(OH)_{2}(s)$ blue ppt

> Upon addition of excess NH₃, ppt dissolves and <u>deep blue solution</u> is formed. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$ deep blue complex

Alternative equations: $Cu^{2+}(aq) + 2OH^{-}(aq) \longrightarrow Cu(OH)_{2}(s)$ $Cu(OH)_{2}(s) + 4NH_{3}(aq) \longrightarrow [Cu(NH_{3})_{4}]^{2+} + 2OH^{-}$

Comments

- Recall that NH_3 is a source of OH^- ions as it is a weak base. $NH_3 + H_2O \Rightarrow NH_4^+ + OH^-$
- Please refer to the Data Booklet (pg 56, Qualitative Analysis Notes) for the observations when NH₃ is added to a solution of Cu²⁺. This would be the immediate observation (testing on QA) instead of Cu solid becoming smaller because of a shifting of position of equilibrium.
- For the equation Cu²⁺(aq) + 2OH⁻(aq) → Cu(OH)₂(s), many students gave 1 mol of OH⁻ instead. Some students missed out the formation of Cu(OH)₂ entirely.
- Although state symbols are not required, it is a good practice to show them in this case since it helps to explain the observations.
- **5(a)(iv)** Upon addition of NH₃, [Cu²⁺] decreases such that it becomes less than 1 mol dm⁻³ (i.e. conditions are no longer standard). Position of equilibrium for Cu²⁺ + 2e⁻ \rightleftharpoons Cu shifts to the left.

 E_{anode} in (a)(ii) decreases and hence <u> E_{cell} becomes more positive</u>.

Comments

- In the equation $E^{\ominus}_{cell} = E^{\ominus}_{cathode} E^{\ominus}_{anode}$, both $E^{\ominus}_{cathode}$ and E^{\ominus}_{anode} are reduction potentials, i.e. the values as found in the Data Booklet. Hence, even though oxidation is taking place in the Cu²⁺/Cu half-cell, the equation that we refer to, to show how E_{anode} is affected, should be the equation that is in the reduction direction, as found in the Data Booklet.
- Students should clearly indicate which equilibrium reaction they are referring to in their answers.

5(b) $\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = -(2)(96500)(+1.60) = -309 \text{ kJ mol}^{-1}$

- When applying $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$, the units for ΔG^{\ominus} is J mol⁻¹ (not kJ mol⁻¹). Answers must include units for ΔG^{\ominus} .
- Many students forgot the minus sign or wrote it at first and omitted it in the final answer.

6(a) <u>ams and msr</u> as they <u>do not follow the general formula $NH_2CH(R)COOH$.</u>

Comments

- Several students were unclear about the structure of an amino acid and incorrectly thought that an amino acid must contain only one amine group and one carboxylic acid group.
- Note that amino acids are organic compounds that contain <u>at least</u> one amine group (–NH₂) and one carboxylic acid group (–COOH). In an α-amino acid, the amine group is attached to the α carbon atom, i.e. the carbon atom that is bonded to the carboxylic acid group. All the 20 amino acids from which proteins are derived from, are α-amino acids with the general structure NH₂CH(R)COOH (with the exception of proline).
- Hence, *msr* is an α -amino acid but is not found in proteins as it lacks a H atom bonded to the α carbon.
- If unsure, students should not use the Greek alphabets α and β in their answers. A number of students mistakenly identified *msr* as a β -amino acid. A better strategy would be to simply describe the structure.



Comments

6(b)

- A dipeptide should contain only two amino acid residues in the correct sequence (i.e. *his-msr*).
- The peptide bond (-CONH-) is an amide group and is neutral. Hence, amides should not be protonated, i.e. structures containing (-CON⁺H₂-) are incorrect.
- By convention, the structure of peptides is reported from the N-terminus on the left to the C-terminus on the right. Therefore, *his* should have a free –NH₃⁺ group and *msr* should have a free –COOH group.



- The –NH groups on the ring, which is part of the R group of *his*, should not be involved in peptide formation.
- Even though the dipeptide was suggested to be of alien origin, all the above conventions have to be followed since the normal three letter code structure for the dipeptide was used.
- 6(c)(i) $pK_b \text{ of } N^{\text{O}} = 14 9.17 = \frac{4.83}{9}$ $pK_b \text{ of } N^{\text{O}} = 14 - 6.00 = \frac{8.00}{8}$

Comments

• Generally well done. Recall that $pK_w = pK_a + pK_b = 14$ (at 298 K).

6(c)(ii) sp³

Comments

- Generally well done.
- N^① has 1 lone pair and 3 bond pairs. Hence N^① has a trigonal pyramidal shape (electron pair geometry is tetrahedral) ⇒ hybridisation of N^① is sp³ (NOT sp²)
- Other incorrect answers include sp3, sp3
- **6(c)(iii)** The lone pair on N^① is located in the sp³ hybrid orbital which has <u>less s character</u> than the lone pair on N^③ which is located in the sp² hybrid orbital. Therefore, N^① lone pair is less strongly attracted to the nucleus and is <u>more available for coordination with a proton</u>.

Comments

- The comparison in the strength of the bases must be with reference to the availability of the lone pair on N atom for coordination <u>with a proton</u>.
- The question already stated that 'the lone pair on N³ is located in the sp² hybrid orbital'. Since the sp² orbital is perpendicular to the unhybridised p orbitals of the atoms forming the 5-membered ring, it is impossible for the lone pair on N³ to be delocalised into the ring.
- **6(c)(iv)** The unhybridised p orbital on N² can overlap with the unhybridised p orbitals of the other atoms in the ring. Therefore the lone pair is <u>delocalised and unavailable for coordination with a proton.</u>

- Generally well done.
- Answers must be with reference to the structure of the 5-membered ring in *his*, i.e. there are no C=O bond in the 5-membered ring.
- Students should be careful with the appropriate usage of terms for their explanations. Resonance stabilisation is used to explain that the overall energy of a molecule will be lowered, usually due to delocalisation of electrons or charge. Usage of the term 'resonance stabilisation' to explain why the lone pair of electrons in N² will not be available for coordination to a H⁺ does not make sense. Similarly, stating that the partial overlap of p orbital on N² leading to formation of a double bond character does not help in explaining basicity of N².



Comments					
•	• For 6(d) : At the maximum buffering capacity, $\frac{[conjugate acid]}{[base]} = 1 \& pH = pK_a$ (or pOH = pK _b).				
•	A common mistake is to use $pH = pK_b$. For 6(f)(ii) : Generally well done.				
6(e	6(e) $n(HCl)$ added = $n(conjugate acid)$ formed = $6/1000 \times 0.1 = 0.0006$ mol $n(fully deprotonated his) remaining = (10/1000 \times 0.1) - 0.0006 = 0.0004 mol$				
	$pH = pK_a + lg ([fully deprotonated his] / [conjugate acid])= 9.17 + lg (0.0004 / 0.0006)= 8.99$				
 <u>Comments</u> After 6.0 cm³ of HC<i>l</i>(aq) was added, a buffer solution containing the fully deprotonated <i>his</i> and its conjugate acid (p<i>K</i>_a = 9.17) was formed. 					
	pK _a = 9.17				
	$ \begin{array}{c} \Theta \\ O \\$				
	fully deprotonated <i>his</i> conjugate acid of fully deprotonated <i>his</i>				
	(For the order of the stepwise protonation of the fully deprotonated his, refer to the comments in 6(f)(i).)				
•	• The amount/ratio of the two components must be calculated before using the buffer equation to				
•	• Many students memorised the Henderson–Hasselbalch equation as: $pH = pK_a + lq ([salt] / [acid])$				
	This led to confusion as to which species is the salt, and which species is the acid.				

A more accurate form of the equation would be:

$$\mathsf{pH} = \mathsf{p}K_{\mathsf{a}} + \mathsf{lg}\left([\mathsf{A}^{-}] / [\mathsf{HA}]\right)$$

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This would make clear where to substitute the protonated species (denominator) and the deprotonated species (numerator).

• Students are reminded of the need for clear presentation of answers.



Comments The lower the pK_b (the higher the K_b), the stronger the base. • pK_b of N^① = 14 - 9.17 = 4.83 pK_b of $-COO^- = 14 - 1.82 = 12.18$ $pK_b \text{ of } N^{3} = 14 - 6.00 = 8.00$ Hence, basicity of $N^{\odot} > N^{\odot} > -COO^{-}$ The fully deprotonated his undergoes a stepwise protonation when titrated against an acid: Ð ⊕ ŅH₃ Ð $\widetilde{N}H_3$ NΗ $\rm NH_2$ [⊖]0. ⊖o ⊖o ö \cap \cap major species at major species at fully deprotonated his first equiv pt (Y) second equiv pt (Z) æ Ð NΗ NH_3 HO Ô major species at third equiv pt