

- In the spaces provided, explain the meanings of the following terms. You may use an equation or diagram where appropriate.

(a) hydrogen bonding

**An unusually strong dipole-dipole interaction that forms when a hydrogen atom is bonded to one of the very electronegative atoms F, O or N.**

(b) colligative properties

**Properties of a solution that depend only upon the number of moles of solute present, not the nature of the solute.**

(c) hypotonic solution

**A solution with lower osmotic pressure than cell fluid.**

(d) isoelectric point

**The pH at which there is no net charge on a molecule containing both acidic and basic groups.**

(e) half life

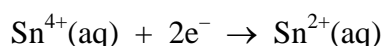
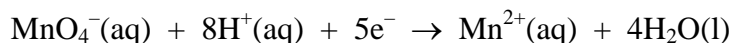
**The time required for the concentration of a reactant to fall to half its initial value. Commonly applied to radioactive materials where it is the time taken for the activity of a sample to fall to half its initial value.**

- Give the oxidation number of carbon in each of the following.

$\text{CF}_2\text{Cl}_2(\text{g})$	<b>+4</b>
$\text{Na}_2\text{C}_2\text{O}_4(\text{s})$	<b>+3</b>
$\text{HCO}_3^-(\text{aq})$	<b>+4</b>
$\text{C}(\text{s})$	<b>0</b>

**Marks****2**

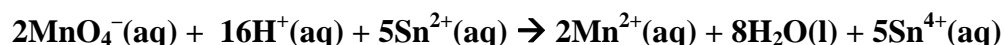
- Consider a voltaic cell that uses the following half-reactions:



Write a balanced equation for the overall reaction.

**3**

**The two cell potentials are +1.51 V ( $\text{MnO}_4^-/\text{Mn}^{2+}$ ) and +0.15 V ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ). The least positive ( $\text{Sn}^{4+}/\text{Sn}^{2+}$ ) is reversed so that it is the oxidation reaction. Combining the half cells in this way gives, after balancing:**



Which species is the oxidising agent?

 **$\text{MnO}_4^-(\text{aq})$** 

Which species is the reducing agent?

 **$\text{Sn}^{2+}(\text{aq})$** 

Calculate the standard cell potential. (Refer to the table of standard reduction potentials.)

**As noted above, the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  half cell is reversed so that its oxidation potential is -0.15 V. Hence, the standard cell potential is:**

$$E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ} + E_{\text{ox}}^{\circ} = (+1.51) + (-0.15) = +1.38 \text{ V}$$

Answer: **+1.38 V**

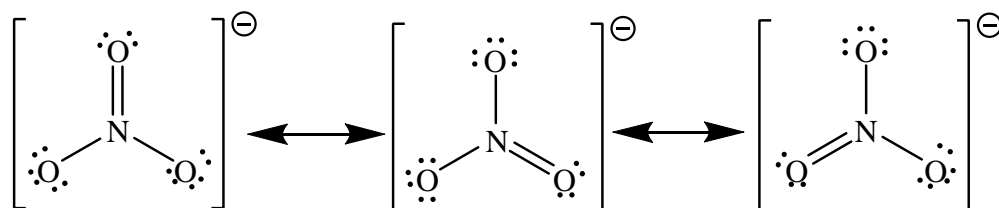
**Marks**  
**9**

- Complete the table below showing the number of valence electrons, the Lewis structure and the VSEPR predicted shape of each of the following species.

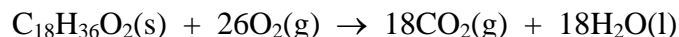
Formula	Number of valence electrons	Lewis structure	Geometry of species
e.g. NH <sub>3</sub>	8	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\   \\ \text{H} \end{array}$	trigonal pyramidal
CH <sub>4</sub>	8	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{H} \\   \\ \text{H} \end{array}$	<b>tetrahedral</b>
CO <sub>2</sub>	16	$\text{:}\ddot{\text{O}}=\text{C}=\ddot{\text{O}}\text{:}$	<b>linear</b>
PF <sub>5</sub>	40	$\begin{array}{c} \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \\   \\ \text{P} \\   \\ \text{:}\ddot{\text{F}}\text{:} \\ \text{:}\ddot{\text{F}}\text{:} \end{array}$	<b>trigonal bipyramidal</b>
NO <sub>3</sub> <sup>-</sup>	24	$\left[ \begin{array}{c} \text{:}\ddot{\text{O}}\text{:} \\    \\ \text{:}\ddot{\text{O}}-\text{N}-\ddot{\text{O}}\text{:} \\   \\ \text{:}\ddot{\text{O}}\text{:} \end{array} \right]^{-}$	<b>trigonal planar</b>

Which one of the species above displays resonance, and how many resonance forms are possible?

**NO<sub>3</sub><sup>-</sup> shows resonance – three forms are possible:**



- Stearic acid,  $C_{18}H_{36}O_2$ , is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:



Calculate  $\Delta H^\circ$  for this reaction given the following heats of formation.

$$\Delta H_f^\circ (C_{18}H_{36}O_2(s)) = -948 \text{ kJ mol}^{-1}, \quad \Delta H_f^\circ (CO_2(g)) = -393 \text{ kJ mol}^{-1} \text{ and}$$

$$\Delta H_f^\circ (H_2O(l)) = -285 \text{ kJ mol}^{-1}$$

Using  $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$ , the heat of the reaction as written is:

$$\begin{aligned} \Delta_{\text{rxn}}H^\circ &= [18\Delta_fH^\circ(CO_2(g)) + 18\Delta_fH^\circ(H_2O(l))] \\ &\quad - [\Delta_fH^\circ(C_{18}H_{36}O_2(s)) + 26\Delta_fH^\circ(O_2(g))] \\ &= [(18 \times -393) + (18 \times -285)] - [(-948) + (26 \times 0)] = -11256 \text{ kJ mol}^{-1} \end{aligned}$$

$\Delta_fH^\circ(O_2(g)) = 0$  for an element already in their standard states.

Answer:  $-11256 \text{ kJ mol}^{-1}$

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the  $\Delta H^\circ$  for the combustion of stearic acid in air given that



Energy must be provided to vaporize the water so the enthalpy of combustion is reduced:

$$\Delta_{\text{comb}}H^\circ = -11256 + (18 \times 44) = -10464 \text{ kJ mol}^{-1}$$

Answer:  $-10464 \text{ kJ mol}^{-1}$

Will  $\Delta S$  be different for the two oxidation reactions? If so, how will it differ and why?

The entropy of  $H_2O(g)$  is greater than that of  $H_2O(l)$  so  $\Delta S$  will be greater. In the oxidation reaction which produces  $H_2O(l)$ , 26 mol of gas are converted into 18 mol of gas so that  $\Delta S$  will be negative. In the oxidation reaction which produces  $H_2O(g)$ , 26 mol of gas are converted into  $(18 + 18) = 36$  mol of gas and  $\Delta S$  will be positive.

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

**The molar mass of stearic acid, C<sub>18</sub>H<sub>36</sub>O<sub>2</sub>, is:**

$$18 \times 12.01 \text{ (C)} + 36 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)} = 284.468$$

**1.0 g therefore contains:**

$$\text{number of moles of stearic acid} = \frac{\text{mass}}{\text{molar mass}} = \frac{1.00}{284.468} = 0.00352 \text{ mol}$$

**As 18 mol of CO<sub>2</sub> are produced for every mole of stearic acid:**

$$\text{number of moles of CO}_2 = 18 \times 0.00352 = 0.0633 \text{ mol}$$

**The molar mass of CO<sub>2</sub> is (12.01 (C) + 2 × 16.00 (O)) = 44.01. The mass of CO<sub>2</sub> is thus:**

$$\text{mass of CO}_2 = \text{number of moles} \times \text{molar mass} = 0.0633 \times 44.01 = 2.78 \text{ g}$$

**Answer: 2.78 g**

- Lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , is produced in the body during normal exercise. It is a monoprotic acid with a  $\text{p}K_a$  of 3.86.
- (a) What is the pH of a 0.10 M water solution of lactic acid?

The reaction table is:

	lactic acid(aq)	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	lactate(aq)	$\text{H}_3\text{O}^+(\text{aq})$
start	0.10	large		0	0
change	-x	-x		+x	+x
equilibrium	0.10-x	large		x	x

As  $\text{p}K_a = -\log_{10}(K_a) = 3.86$ ,  $K_a = 10^{-3.86}$  and:

$$K_a = \frac{[\text{lactate}(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{lactic acid}(\text{aq})]} = \frac{(x)(x)}{(0.10 - x)} = \frac{x^2}{(0.10 - x)} = 10^{-3.86}$$

As  $K_a$  is very small, x is tiny and  $0.10 - x \sim x$ . Hence,

$$K_a \sim \frac{x^2}{(0.10)} = 10^{-3.86} \text{ or } x^2 = (0.10) \times (10^{-3.86}) \text{ so } x = [\text{H}_3\text{O}^+(\text{aq})] = 3.72 \times 10^{-3} \text{ M}$$

As  $\text{pH} = -\log_{10}([\text{H}_3\text{O}^+(\text{aq})])$ :

$$\text{pH} = -\log_{10}(3.72 \times 10^{-3}) = 2.43$$

Answer: 2.43

- (b) Calculate the pH of the solution formed when 0.02 mol of  $\text{Ca}(\text{OH})_2(\text{s})$  is added to 1.0 L of 0.10 M lactic acid.

1.0 L of 0.10M lactic acid contains 0.10 mol of acid.

$\text{Ca}(\text{OH})_2$  is a strong base. It will dissociate completely to give  $2\text{OH}^-(\text{aq})$  for every 1 mole of  $\text{Ca}(\text{OH})_2$ .  $(2 \times 0.02) = 0.04$  mol of  $\text{OH}^-(\text{aq})$  will be produced. This will neutralize 0.04 mol of the acid leaving  $(0.10 - 0.04) = 0.06$  mol of acid. Assuming that the volume does not change from the addition of the solid,  $[\text{lactic acid}] = 0.060$  M. The neutralization produces lactate anion with  $[\text{lactate}] = 0.040$  M.

The solution now contains acid and its conjugate base. It is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation can be used:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = 3.86 + \log_{10}\left(\frac{0.040}{0.060}\right) = 3.86$$

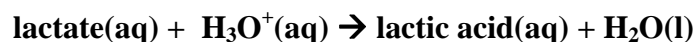
Answer: 3.86

ANSWERS CONTINUES ON THE NEXT PAGE

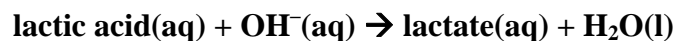
(c) Using equations, comment on how the final solution in (b) will respond to additions of small amounts (e.g. less than 0.01 mol) of acid or base in comparison to additions of the same amounts of acid or base to 1 L of water.

**The solution in (b) will act as a buffer. As it contains both an acid (lactic acid) and a base (lactate), it can react with both added base and acid to maintain a near constant pH.**

**Added  $\text{H}_3\text{O}^+$  will be consumed by the reaction of the lactate anion:**



**Added  $\text{OH}^-$  will be consumed by the reaction of the lactic acid:**

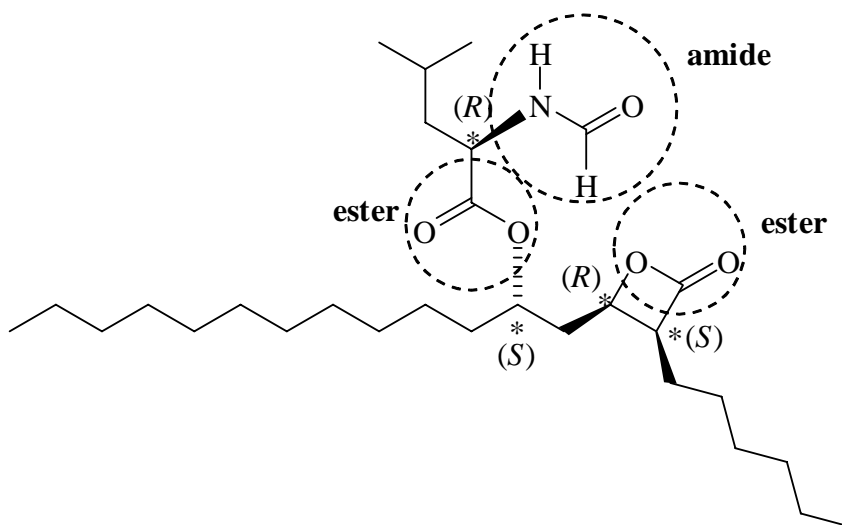


**As long as the amounts of lactic acid and lactate are large in comparison to the added acid or base, the pH is approximately constant and is described by the Henderson-Hasselbalch equation.**

**If acid or base is added to water, the  $[\text{H}_3\text{O}^+(\text{aq})]$  or  $[\text{OH}^-(\text{aq})]$  will change according to the amount added and the pH will change rapidly.**

**Marks**  
**6**

- Orlistat (shown below) is a drug for obesity management which acts by inhibiting the absorption of dietary fats.



Is it likely to be soluble in water? Why?

**The molecule contains long-chain hydrocarbon areas which are hydrophilic. Although oxygen atoms are present, there are no O-H groups to allow H-bonding. The molecule is thus unlikely to be soluble in water.**

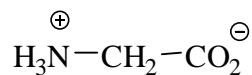
Indicate on the above structure all stereogenic centres. Select one of these centres and clearly assign its stereochemical configuration.

Name the functional groups present in orlistat.

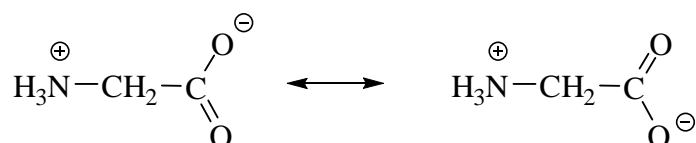
**Ester  $\times$  2 and amide (see structure).**



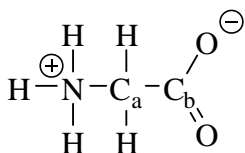
- Glycine,  $\text{NH}_2\text{CH}_2\text{COOH}$ , is the simplest of all naturally occurring amino acids. The  $\text{p}K_a$  of the acid group is 2.35 and the  $\text{p}K_a$  associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4.



Use your structure to illustrate the concept of resonance.



What are the hybridisation states and geometries of the two carbon atoms and the nitrogen atom in glycine?



**N has 4 bonds and no lone pairs:  $sp^3$  with a tetrahedral geometry.**

**$\text{C}_a$  has 4 bonds and no lone pairs:  $sp^3$  with a tetrahedral geometry.**

**$\text{C}_b$  has 3 bonds and no lone pairs:  $sp^2$  with a trigonal planar geometry.**

Propionic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , has a melting point of  $-20.7\text{ }^\circ\text{C}$  while glycine has a melting point of  $292\text{ }^\circ\text{C}$ . Suggest a reason why these two molecules have such different melting points.

**The major intermolecular force in glycine is ionic bonding between the positively and negatively charged ends of the molecule. The major intermolecular force in propionic acid is hydrogen bonding between the carboxylic acid groups. Ionic bonding is much stronger than H-bonding so glycine has a much higher melting point.**

**Marks**  
**6**

- Alanine ( $R = \text{CH}_3$ ) and lysine ( $R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) are two common amino acids. Using *ala* and *lys* to represent the two amino acids, represent all constitutional isomers of the tripeptide formed from one *ala* and two *lys* units.

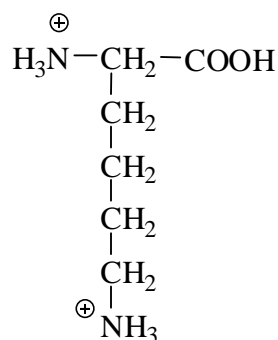
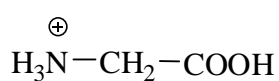
**Three tripeptides are possible: *ala-lys-lys*, *lys-ala-lys* and *lys-lys-ala***

Comment, giving your reason, on whether the tripeptide(s) will be acidic, neutral or basic in character.

**Lysine has a basic, amine sidechain ( $R = \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ) whilst alanine has a neutral sidechain ( $R = \text{CH}_3$ ). The tripeptide(s) will thus be basic.**

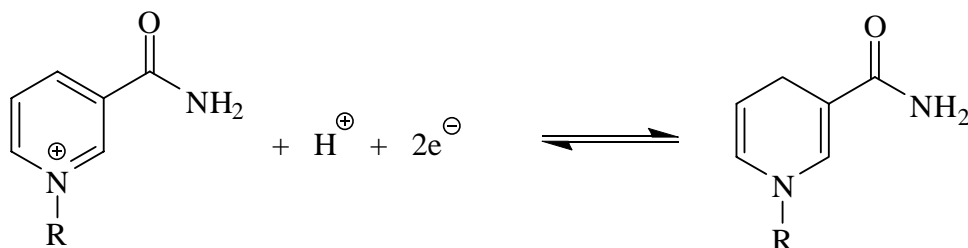
Draw the constitutional formulas, indicating the correct ionic state, of the products formed from acid hydrolysis of one of your tripeptides.

**Each tripeptide will be hydrolysed to give alanine and lysine. In acid, these will be present with the basic amine groups (including the sidechain of lysine) and the carboxylic acid groups in the protonated forms:**



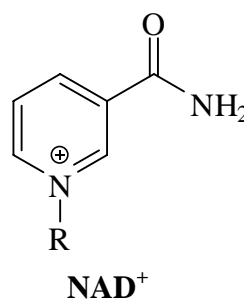
Marks  
4

- NAD<sup>+</sup> and NADH are coenzymes used by animals in oxidation and reduction reactions. They are related by the following half-reactions.

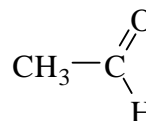


Which of these coenzymes is used in the biological oxidation of ethanol, CH<sub>3</sub>CH<sub>2</sub>OH?

An oxidizing agent is itself reduced. As shown in the equation, it is NAD<sup>+</sup> which is reducible.



What is the product of the biological oxidation of ethanol, CH<sub>3</sub>CH<sub>2</sub>OH?



Which of NAD<sup>+</sup> and NADH is aromatic? Give reasons for your answer.

**NAD<sup>+</sup> is aromatic. It is cyclic, planar, conjugated, and has  $4n+2$   $\pi$  electrons. NADH is not fully conjugated and is therefore not aromatic.**

- Benzoic acid has a low solubility in water at pH 7, but is very soluble in aqueous solutions of greater pH. Explain this observation, using chemical equations where appropriate.

2

**Benzoic acid has a low solubility in water because of the relatively large hydrophobic aromatic ring. It is a weak acid so exists primarily as the undissociated acid at pH 7. At high pH, it can react with OH<sup>-</sup> ions to form the benzoate ion. This species is water soluble because it is charged and hence is easily solvated by the polar water molecules.**

