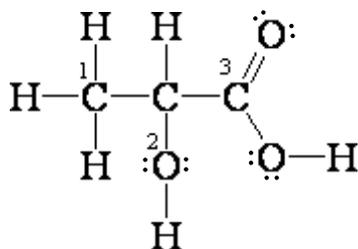|	**Marks**
• The partial Lewis structure of lactic acid, the molecule that forms in muscle during exercise, is shown below. Complete the Lewis structure of lactic acid by drawing the non-bonded electron pairs around the relevant atoms.	**7**

2

Complete the following table.

2

Atom	Geometric arrangement of the groups around the atom	Hybridisation of atom
^1C	**tetrahedral**	sp^3
^2O	**bent**	sp^3
^3C	**trigonal planar**	sp^2

Name three types of intermolecular interactions expected of lactic acid.

3

- **hydrogen bonding (alcohol and acid groups)**

- **dipole-dipole interactions (alcohol and acid groups)**

- **dispersion forces (all groups but the only interactions for methyl group)**

- Some micro-organisms thrive under warm, acidic conditions where sulfuric acid is produced as a metabolic by-product from the reaction between sulfur (S), water and oxygen (O_2). Write a balanced equation for this reaction.

$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(l)$

Calculate the volume of oxygen that is required to react to completion with 0.0655 g of sulfur at 1.00 atm and 55 °C.

The number of moles of sulfur in 0.0655 g is:

$$\textbf{number of moles} = \frac{\textbf{mass}}{\textbf{atomic mass}} = \frac{\textbf{0.0655 g}}{\textbf{32.07 g mol}^{-1}} = \textbf{0.00204 mol}$$

From the chemical equation, *two* moles of S react with *three* moles of O_2. Therefore, 1.5×0.00204 mol = 0.00306 mol of oxygen is required.

Using the ideal gas law, *PV = nRT*, the volume of this number of moles of O_2 can be calculated. As the pressure = 1.00 atm, the corresponding value of *R* to be used is 0.08206 L atm K^{-1} mol^{-1}. *T* = 55 °C = (55 + 273) K = 328 K.

$$V = \frac{nRT}{P} = \frac{(\textbf{0.00306 mol})(\textbf{0.08206 L atm K}^{-1} \textbf{mol}^{-1})(\textbf{328 K})}{\textbf{1.00 atm}}$$
$$= \textbf{0.0825 L or 82.5 mL}$$

ANSWER: **0.0825 L or 82.5 mL**

Calculate the pH of the final solution if the reaction is carried out in 20.0 L of water. Assume that the sulfuric acid fully dissociates.

***Two* moles of H_2SO_4 are produced for every *two* moles of sulfur used. The number of moles of H_2SO_4 produced is therefore 0.00204 mol.**

If the H_2SO_4 completely dissociates into H^+ and SO_4^{2-}, *two* moles of H^+ are produced for every *one* mole of H_2SO_4. The number of moles of H^+ is therefore 0.00408 mol.

This number of moles is dissolved in 20.0 L of water, the concentration of H^+ is therefore:

$$\textbf{concentration} = \frac{\textbf{number of moles}}{\textbf{volume}} = \frac{\textbf{0.00408 mol}}{\textbf{20.0 L}} = \textbf{0.000204 M}$$

Using the definition of pH,

$$\textbf{pH} = -\textbf{log}_{10}[\textbf{H}^+] = -\textbf{log}_{10}(\textbf{0.000204}) = \textbf{3.69}$$

ANSWER: **3.69**

Marks
8

- Shown here are the classical and the zwitterionic forms of the amino acid leucine.
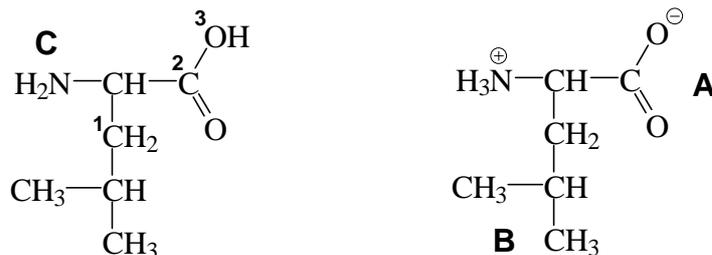
List the types of intermolecular interactions in which each of the indicated sites (**A**, **B** and **C**) in leucine could be involved.
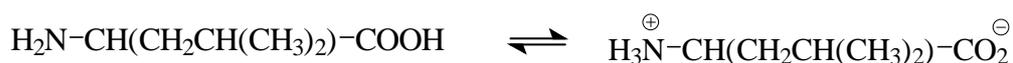
| **A** | **ion-ion, ion-dipole, ion-induced dipole** |

| **B** | **dispersion** |

| **C** | **hydrogen bonding, dipole-dipole, dipole-induced dipole** |

Provide the requested information for each of the indicated atoms in leucine.

Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry/shape of σ-bonding electron pairs around the atom
^{1}C	**tetrahedral**	sp^3	**tetrahedral**
^{2}C	**trigonal planar**	sp^2	**trigonal planar**
^{3}O	**tetrahedral**	sp^3	**bent**

Given that the pK_a of the carboxylic acid group of leucine is 2.32 and the pK_b of the amine group is 4.24, do you expect the classical or the zwitterionic form to predominate when leucine is dissolved in water? In other words, does the following equilibrium lie to the right or left? Show your reasoning.

$$H_2N\text{–}CH(CH_2CH(CH_3)_2)\text{–}COOH \rightleftharpoons \overset{\oplus}{H_3N}\text{–}CH(CH_2CH(CH_3)_2)\text{–}\overset{\ominus}{CO_2}$$

The equilibrium for the K_a of the acid group is:

    H₂N-CHR-COOH ⇌ H₂N-CHR-COO⁻ + H⁺

for which:

$$K_{a(COOH)} = \frac{[\text{H}^+][\text{H}_2\text{NCHR} - \text{COO}^-]}{[\text{H}_2\text{NCHR} - \text{COOH}]} = 10^{-2.32}$$

The equilibrium for protonation of the amine group is:

    H₂N-CHR-COO⁻ + H⁺ ⇌ H₃N⁺-CHR-COO⁻

for which:

$$K = \frac{[H_3N^+ - CHR - COO^-]}{[H_2NCHR - COO^-][H^+]} = \frac{1}{K_{a(NH_3^+)}} = \frac{1}{10^{-9.76}} = 10^{+9.76}$$

in which pK_a + pK_b = 14 has been used.

The equilibrium for formation of the zwitterionic form in the question is:

   H$_2$N-CHR-COOH $\rightleftharpoons$ H$_3$N$^+$-CHR-COO$^-$

for which:

$$K' = \frac{[H_3N^+ - CHR - COO^-]}{[H_2NCHR - COOH]} = \frac{K_{a(COOH)}}{K_{a(NH_3^+)}} = 10^{-2.32} \times 10^{+9.76} = 10^{7.44}$$

$$\gg 1$$

As the equilibrium constant >> 1, the equilibrium lies far to the right and so the zwitterionic form dominates.

Marks
5

- Consider the following equation.

$$HBrO(aq) + NH_3(aq) \rightleftharpoons BrO^-(aq) + NH_4^+(aq)$$

Name all of the species in this equation.

HBrO	**hypobromous acid**
BrO⁻	**hypobromite ion**
NH₃	**ammonia**
NH₄⁺	**ammonium ion**

Complete the following table by giving the correct pK_a or pK_b value where it can be calculated. Mark with a cross (✗) those cells for which insufficient data have been given to calculate a value.

Species	HBrO	NH₃	BrO⁻	NH₄⁺
pK_a of acid	8.64	✗	✗	**9.24**
pK_b of base	✗	4.76	**5.36**	✗

Determine on which side (left or right hand side) the equilibrium for the reaction above will lie. Provide a brief rationale for your answer.

The reaction is the sum of the acid-base equilibra for HBrO and NH₃:

$HBrO(aq) \rightarrow H^+(aq) + BrO^-(aq)$ **$K_a(HBrO) = 10^{-8.64}$**

$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$ **$K_a(NH_3) = \dfrac{1}{K_a(NH_4^+)} = 10^{+9.24}$**

───

$HBrO(aq) + NH_3(aq) \rightarrow BrO^-(aq)$ **$K = K_a(HBrO) \times K_a(NH_3)$**

───
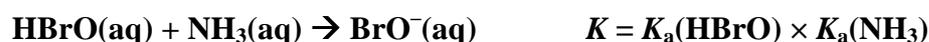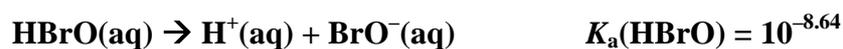
Hence, $K = (10^{-8.64}) \times (10^{+9.24}) = 10^{+0.64} = 4.4$. As $K > 1$, the reaction favours products.

|	Marks
• Glycine, NH_2CH_2COOH, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The pK_a of the acid group is 2.35 and the pK_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.	5

As pH = 7.4 is higher than the pK_a of the acid group, -COOH, it will exist primarily in its deprotonated, conjugate base form, -COO⁻.

As pH = 7.4 is lower than the pK_a of the amino group, -NH$_2$, it will exist primarily in its protonated form, -NH$_3^+$.

Glycine will exist in the uncharged, zwitterionic form: $\overset{\oplus}{H_3N}-CH_2-COO^{\ominus}$

Describe the hybridisation of the two carbon atoms and the nitrogen atom in glycine and the geometry of the atoms surrounding these three atoms.
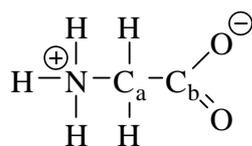
The structure is: **N has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.**

C$_a$ has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.

C$_b$ has 3 bonds and no lone pairs: sp^2 with a trigonal planar arrangement.

Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

Glycine with a positively and a negatively charged end. There is therefore ionic bonding between the molecules leading to strong intermolecular forces.

- The molecular structure of nicotine, the addictive component of tobacco, is shown below.
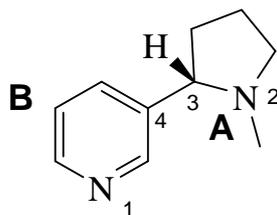
List the types of intermolecular interactions that each of the following sites on nicotine would be involved in when it is dissolved in water.

A – H bonding and dipole-dipole interactions

| **B – dispersion forces and dipole-induced dipole** |
|---|

Provide the requested information for each of the indicated atoms in nicotine.

Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry around the atom
N-1	**trigonal planar**	sp^2	**bent (~120°)**
N-2	**tetrahedral**	sp^3	**trigonal pyramidal**
C-3	**tetrahedral**	sp^3	**tetrahedral**
C-4	**trigonal planar**	sp^2	**trigonal planar**

The pK_b of N-1 is 10.88 and the pK_b of N-2 is 5.98. Draw the structure of the predominant form of nicotine that exists in the human body at pH 7.4.

For N-1, the pK_a of the protonated form (the conjugate acid) is (14.00 – 10.88) = 3.12. As the pH is *higher* than the pK_a, the conjugate acid is deprotonated: *very little protonation occurs*.

For N=2, the pK_a of the protonated form is (14.00 – 5.98) = 8.02. As the pH is *lower* than the pK_a, the conjugate acid form dominates: protonation occurs.
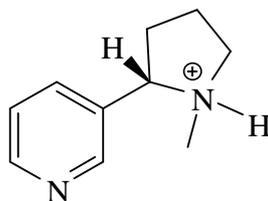
- Lithium salts, especially lithium carbonate, are commonly used in the treatment of bipolar disorder. Write the net ionic equation for the reaction which occurs between lithium carbonate and hydrochloric acid in the stomach.

$Li_2CO_3(s) + 2H^+(aq) \rightarrow 2Li^+(aq) + H_2O(l) + CO_2(g)$

Lithium orotate (as a monohydrate salt, $LiC_5H_3N_2O_4 \cdot H_2O$) is a controversial alternative formulation sold in some health food stores. The orotate ion is the conjugate base of orotic acid, whose structure is shown below.
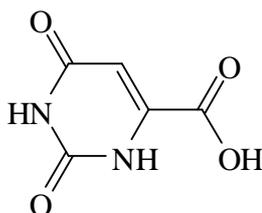
orotic acid

Like the carbonate, lithium orotate is taken orally. Using an equation, comment on any differences between the form in which lithium is bioavailable from these two lithium salts.
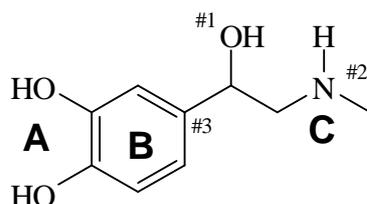
When lithium orotate, $LiC_5H_3N_2O_4$, dissolves in water, it forms Li^+(aq) ions and orotate ions:

   $LiC_5H_3N_2O_4(s) \rightarrow Li^+(aq) + C_5H_3N_2O_4^-(aq)$
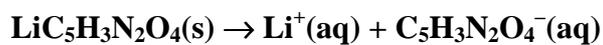
Both lithium carbonate and lithium orotate thus give rise to the same form of lithium, Li^{2+}(aq), when taken orally.

**Marks
8**

•   The molecular structure of adrenaline (epinephrine), a hormone involved in the "fight or flight" response, is shown below.

List the types of intermolecular interactions that each of the following sites on adrenaline would be involved in if dissolved in water.

A   H-bonding, dipole-dipole, dispersion forces

B   dispersion forces

C   H-bonding, dipole-dipole, dispersion forces

Pharmaceuticals with amine groups are frequently supplied as their "hydrochloride salts". Draw the structure that would result if adrenaline were reacted with one equivalent of HCl. What **additional** intermolecular forces would be present if this form of adrenaline were dissolved in water?
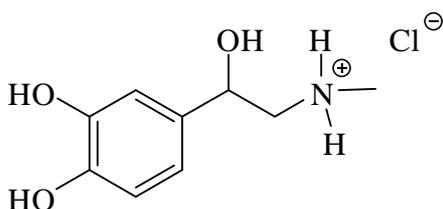
With this form present, ion-dipole interactions would be introduced.

Provide the requested information for each of the indicated sites on adrenaline.

| Atom	Geometric arrangement of the electron pairs around the atom	Hybridisation of the atom	Geometry around the atom	Approximate angles around the atom
#1O	**tetrahedral**	sp^3	**bent**	**109°**
#2N	**tetrahedral**	sp^3	**trigonal pyramidal**	**109°**
#3C	**trigonal planar**	sp^2	**trigonal planar**	**120°**

- Glycine, NH_2CH_2COOH, is the simplest of all naturally occurring amino acids. The pK_a of the acid group is 2.35 and the pK_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.
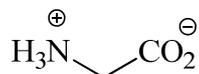
This pH is much *greater* than the pK_a value of the acid group: it is *deprotonated*.

This pH is much *lower* than the pK_a value of the amino group: it is *protonated*.

Use your structure to illustrate the concept of resonance.
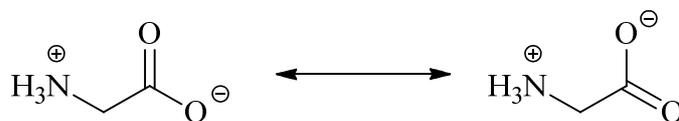
What are the hybridisation states and geometries of the two carbon atoms and the nitrogen atom in glycine?

The carbon on the acid group is *sp^2* hybridised and the geometry is trigonal planar.

The carbon on the CH$_2$ group is *sp^3* hybridised and the geometry is tetrahedral.

The nitrogen is *sp^3* hybridised and the geometry is tetrahedral.

Propionic acid, CH_3CH_2COOH, has a melting point of –20.7 °C while glycine has a melting point of 292 °C. Suggest a reason why these two molecules have such different melting points.

Propionic acid has strong hydrogen bonds, giving it a relatively high melting point.

However, glycine has very strong ionic bonds between the NH$_3^+$ and CO$_2^-$ groups giving it *very* high melting point.

	Marks
• Explain the terms '*weak*' and '*strong*' and the terms '*dilute*' and '*concentrated*' in the context of acids and bases.	**2**

A weak acid or base is one which only partially dissociates in water:
    e.g. $CH_3COOH(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$

A strong acid or base is one which completely dissociates in water:
    e.g. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Concentrated and dilute are terms that can be used in reference to any solute, describing the number of moles of solute relative to the volume of solvent. A concentrated solution has a high solute : solvent ratio, whilst a dilute solution has a low solute:solvent ratio.