**CHEM1611**  
**2004-J-3**  
**June 2004**

- Siderophores (from the Greek meaning ‘iron carriers’) are organic molecules produced by microorganisms to provide essential Fe$^{3+}$ required for growth. The functional group (the group which binds Fe$^{3+}$) of siderophores is shown below as tautomers I and II. Complete the table below, relating to the molecular geometry about the specified atoms in I and II.

  ![Siderophore structures](image)

<table>
<thead>
<tr>
<th>Atom</th>
<th>Geometric arrangement of the electron pairs around the atom</th>
<th>Hybridisation of atom</th>
<th>Geometry of bonding electron pairs around atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$C</td>
<td>tetrahedral</td>
<td>$sp^3$</td>
<td>tetrahedral</td>
</tr>
<tr>
<td>$^2$N</td>
<td>tetrahedral</td>
<td>$sp^3$</td>
<td>trigonal pyramidal</td>
</tr>
<tr>
<td>$^3$C</td>
<td>trigonal planar</td>
<td>$sp^2$</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>$^4$O</td>
<td>tetrahedral</td>
<td>$sp^3$</td>
<td>bent</td>
</tr>
<tr>
<td>$^5$N</td>
<td>trigonal planar</td>
<td>$sp^2$</td>
<td>bent</td>
</tr>
</tbody>
</table>

Desferal is a siderophore-based drug that is used in humans to treat iron-overload. One molecule of Desferal (molecular formula: $C_{25}H_{48}O_8N_6$) can bind one Fe$^{3+}$ ion. A patient with iron-overload had an excess of 0.637 mM Fe$^{3+}$ in his bloodstream. Assuming the patient has a total blood volume of 5.04 L, what mass of Desferal would be required to complex all of the excess Fe$^{3+}$?

In 5.04 L, the number of moles of Fe$^{3+}$ is given by the concentration $\times$ volume:

$$\text{moles of Fe}^{3+} = (0.637 \times 10^{-3} \text{ mol L}^{-1}) \times (5.04 \text{ L}) = 3.2105 \times 10^{-3} \text{ mol}$$

As each desferal molecule binds one Fe$^{3+}$, this is also the number of moles of desferal that is required. The molar mass of desferal is:

$$\text{molar mass} = (25\times12.01 \text{ (C)} + 48\times1.008 \text{ (H)} + 8\times16.00 \text{ (O)} + 6\times14.01 \text{ (N)}) \text{ g mol}^{-1}$$

$$= 560.964 \text{ g mol}^{-1}$$

The mass of desferal required is then the number of moles $\times$ molar mass:

$$\text{mass of desferal} = (3.2105 \times 10^{-3} \text{ mol}) \times (560.964 \text{ g mol}^{-1}) = 1.80 \text{ g}$$

**ANSWER:** 1.80 g

**THIS QUESTION CONTINUES ON THE NEXT PAGE**
Given that haemoglobin contains 4 Fe atoms per molecule and its concentration in blood is 15 g per 100 mL, calculate the total mass of Fe in the patient’s blood before being treated with Desferal. (The molar mass of haemoglobin is $6.45 \times 10^4$ g mol$^{-1}$.)

In 5.04 L, the total mass of haemoglobin is $15 \times (5.04 \times 10^3 / 100) = 756$ g. If the molar mass is $6.45 \times 10^4$ g mol$^{-1}$, this corresponds to

$$\text{moles of haemoglobin} = \frac{\text{mass}}{\text{molar mass}} = \frac{756 \text{ g}}{(6.45 \times 10^4 \text{ g mol}^{-1})} = 0.0117 \text{ mol}$$

As haemoglobin contains 4 Fe atoms, the number of moles of Fe is $4 \times 0.0117$ mol = 0.0469 mol. There is also 3.2105 mol of free Fe$^{3+}$ present (from 2004-J-3) so the total number of moles of Fe is $(0.0469 + (3.2105 \times 10^{-3}))$ mol = 0.050 mol.

The mass of Fe is given by moles $\times$ atomic mass:

$$\text{mass of Fe} = (0.050 \text{ mol}) \times (55.85 \text{ g mol}^{-1}) = 2.80 \text{ g}$$

ANSWER: 2.80 g
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 (O₂). 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:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{0.0655 \text{ g}}{32.07 \text{ g mol}^{-1}} = 0.002042 \text{ mol}$$

Three moles of O₂ are required for every two moles of S. Hence the number of moles of O₂ required is:

$$\text{number of moles} = \frac{3}{2} \times 0.002042 \text{ mol} = 0.003064 \text{ mol}$$

The volume of this number of moles of gas at 1.00 atm and 55 °C (= 328 K) is given by the ideal gas law, $$pV = nRT$$, so,

$$V = \frac{nRT}{p} = \frac{(0.003064 \text{ mol})(0.008206 \text{ L atm K}^{-1} \text{ mol}^{-1})}{1.00 \text{ atm}} = 0.0825 \text{ L}$$

(Note the use of R = 0.08206 L atm K⁻¹ mol⁻¹ as pressure is given in atmospheres leading to an answer in litres)

ANSWER: 0.0825 L

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 H₂SO₄ is produced from every two moles of S. Therefore, the number of moles of H₂SO₄ is just 0.002042 mol. Every mole of H₂SO₄ produces two moles of H⁺. Therefore, the number of moles of H⁺ is

$$\text{number of moles} = 2 \times 0.002042 \text{ mol} = 0.004084 \text{ mol}$$

As the reaction is carried out in 20.0 L of water, the concentration of H⁺ is:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.004084 \text{ mol}}{20.0 \text{ L}} = 0.0002042 \text{ mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE
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.

From the definition of pH:

\[ \text{pH} = \text{pH} = -\log_{10}[H^+] = -\log_{10}(0.0002042) = 3.69 \]

ANSWER: 3.69

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY
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.

\[
\text{H}_2\text{N}-\text{CH(CH}_2\text{CH(CH}_3\text{)}_2\text{)}-\text{COOH} \; \rightleftharpoons \; \text{H}_3\text{N}^-\text{CH(CH}_2\text{CH(CH}_3\text{)}_2\text{)}-\text{CO}_2^-
\]

The equilibrium for the $K_a$ of the acid group is:

\[
\text{H}_2\text{N}-\text{CHR-COOH} \; \rightleftharpoons \; \text{H}_2\text{N}-\text{CHR-COO}^- + \text{H}^+
\]

for which:

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

The equilibrium for protonation of the amine group is:

\[
\text{H}_2\text{N}-\text{CHR-COO}^- + \text{H}^+ \; \rightleftharpoons \; \text{H}_3\text{N}^+\text{-CHR-COO}^-
\]

for which:

\[
K = \frac{[\text{H}_3\text{N}^+\text{-CHR-COO}^-]}{[\text{H}_2\text{NCHR-COO}^-][\text{H}^+]} = \frac{1}{K_{a(\text{NH}_3^+)}[\text{H}^+]} = \frac{1}{10^{-9.76}} = 10^{9.76}
\]

in which $pK_a + pK_b = 14$ has been used.

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

\[
\text{H}_2\text{N}-\text{CHR-COOH} \; \rightleftharpoons \; \text{H}_2\text{N}^+\text{-CHR-COO}^- + \text{H}^+
\]

for which:

\[
K' = \frac{[\text{H}_2\text{N}^+\text{-CHR-COO}^-][\text{H}^+]}{[\text{H}_2\text{NCHR-COOH}]} = \frac{K_{a(\text{COOH})}}{K_{a(\text{NH}_3^+)}} = 10^{-2.32} \times 10^{9.76} = 10^{7.44} \gg 1
\]

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