1. (a) \( \text{CH}_3(\text{CH}_2)_{14}\text{COOH}(s) + 23\text{O}_2(g) \rightarrow 16\text{CO}_2(g) + 16\text{H}_2\text{O}(l) \)

Using \( \Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - n\Delta_fH^\circ(\text{reactants}) \) and \( \Delta_fH^\circ(\text{O}_2(g)) = 0 \):

\[
\Delta_{\text{comb}}H^\circ = [16 \times \Delta_fH^\circ(\text{CO}_2(g)) + 6 \times \Delta_fH^\circ(\text{H}_2\text{O}(l))] - [\Delta_fH^\circ(\text{palmitic acid})]
\]

As the combustion is an exothermic process, \( \Delta_{\text{comb}}H^\circ = -9980 \text{ kJ mol}^{-1} \).

Therefore:

\[
[16 \times -393.5 + 6 \times -285.8] \text{ kJ mol}^{-1} - \Delta_fH^\circ(\text{palmitic acid}) = -9980 \text{ kJ mol}^{-1}
\]

or

\[
\Delta_fH^\circ(\text{palmitic acid}) = -889 \text{ kJ mol}^{-1}
\]

(b) \( \text{CH}_3(\text{CH}_2)_{14}\text{COOH} \equiv \text{C}_{16}\text{H}_{32}\text{O}_2 \). The molar mass of palmitic acid is

\[
(16 \times 12.01 \text{ (C)} + 32 \times 1.008 \text{ (H)} + 2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 256.416 \text{ g mol}^{-1}
\]

So,

\[
\Delta_{\text{comb}}H^\circ = -9980 \text{ kJ mol}^{-1} \quad \text{or} \quad \frac{-9980 \text{ kJ mol}^{-1}}{256.416 \text{ g mol}^{-1}} = -38.9 \text{ kJ g}^{-1}
\]

2. \( \text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightleftharpoons 6\text{CO}_2(g) + 6\text{H}_2\text{O}(l) \)

(a) Using \( \Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - n\Delta_fH^\circ(\text{reactants}) \) and as \( \Delta_fH^\circ(\text{O}_2(g)) \) for an element in its standard state:

\[
\Delta_{\text{rxn}}H^\circ = [6 \Delta_fH^\circ(\text{CO}_2(g)) + 6\Delta_fH^\circ(\text{H}_2\text{O}(l))] - [\Delta_fH^\circ(\text{C}_6\text{H}_{12}\text{O}_6(g)) + 6\Delta_fH^\circ(\text{O}_2 (g))]
\]

\[
= [[(6 \times -393) + 6 \times -285)] - [(-1285) + 6 \times 0)] \text{ kJ mol}^{-1} = -2783 \text{ kJ mol}^{-1}
\]

(b) Using \( \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \),

\[
\Delta G^\circ = (-2783 \times 10^3 \text{ J mol}^{-1}) - ((298 \text{ K}) \times 181 \text{ J K}^{-1} \text{ mol}^{-1})
\]

\[
= -2837000 \text{ J mol}^{-1} = -2837 \text{ kJ mol}^{-1}
\]

Note that \( \Delta S^\circ \) is expressed in J K\(^{-1}\) mol\(^{-1}\) so that \( \Delta H^\circ \) must be converted from kJ mol\(^{-1}\) into J mol\(^{-1}\) (by multiplying by \( 10^3 \)).

(c) The equilibrium constant in terms of concentrations, \( K_c \), is given by

\[
K_c = \frac{[\text{CO}_2(g)]^6}{[\text{O}_2(g)]^6}
\]

As \( \text{H}_2\text{O} \) is formed as a liquid and \( \text{C}_6\text{H}_{12}\text{O}_6(s) \) is a solid, they do not appear in the equilibrium expression.

In this reaction, there is no change in the number of moles of gas so \( K_p = K_c \). The equilibrium constant is related to \( \Delta G^\circ \) using \( \Delta G^\circ = -RT\ln K_p \). Hence
This gives a very large value for the equilibrium constant, consistent with the large negative value for Δ\(\text{G}^\circ\). The reaction essentially goes to completion.

(d) Oxidation of 1 mole of glucose produces -2837 kJ mol\(^{-1}\). If ATP synthesis is 41% efficient then the amount of usable energy is 0.41 \(\times\) 2837 = 1163 kJ mol\(^{-1}\). To produce 1 mole of ADP requires 30.5 kJ mol\(^{-1}\) so 1200 kJ will produce:

\[
\text{number of moles} = \frac{1200 \text{ kJ}}{30.5 \text{ kJ mol}^{-1}} = 38 \text{ mol}
\]

3. \[Q = \frac{[\text{SO}_3(g)]^2}{[\text{SO}_3(g)]^2[\text{O}_2(g)]} = \frac{(3.00)^2}{(2.00)^2(1.50)} = 1.5.\]

As \(Q < 4.35\), the reaction proceeds to the right, producing more \(\text{SO}_3(g)\).

4. The paper bag captures exhaled \(\text{CO}_2\) so that the air that is taken in has a higher \(\text{CO}_2\) concentration. As a result, the first equilibrium shifts to the right to reduce the \([\text{CO}_2]\), producing more \(\text{H}_2\text{CO}_3(aq)\). As a result of the increase in \([\text{H}_2\text{CO}_3(aq)]\), the second equilibrium also shifts to the right. \([\text{H}_3\text{O}^+(aq)]\) thus increases, decreasing the pH.

\[\text{CO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{CO}_3(aq)\]
\[\text{H}_2\text{CO}_3(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{HCO}_3^-(aq)\]

5. (a) As acetic acid is a weak acid, \([\text{H}_3\text{O}^+]\) must be calculated:

<table>
<thead>
<tr>
<th></th>
<th>CH(_3)COOH</th>
<th>H(_2)O</th>
<th>(\rightleftharpoons)</th>
<th>H(_3)O(^+)</th>
<th>CH(_3)COO(^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.20</td>
<td>large</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.20 - x</td>
<td>large</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant \(K_a\) is given by:

\[
K_a = \frac{[\text{H}_3\text{O}^+(aq)][\text{CH}_3\text{COO}^-(aq)]}{[\text{CH}_3\text{COOH}(aq)]} = \frac{x^2}{(0.20 - x)}
\]

As \(pK_a = 4.76 = -\log_{10}K_a\) so \(K_a = 10^{-4.76}\). As \(K_a\) is very small, \(0.20 - x \sim 0.20\) and hence:

\[x^2 = 0.20 \times 10^{-4.76} \quad \text{or} \quad x = 0.0019 \text{ M} = [\text{H}_3\text{O}^+(aq)]\]

Hence, the pH is given by:

\[
\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(aq)] = -\log_{10}[0.0019] = 2.7
\]
(b) As CH₃COO⁻ is a weak base, [OH⁻] must be calculated in a similar way:

<table>
<thead>
<tr>
<th></th>
<th>CH₃COO⁻</th>
<th>H₂O</th>
<th>⇌</th>
<th>OH⁻</th>
<th>CH₃COOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.20</td>
<td>large</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>change</td>
<td>-x</td>
<td>negligible</td>
<td>+x</td>
<td>+x</td>
<td></td>
</tr>
<tr>
<td>final</td>
<td>0.20 − x</td>
<td>large</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

The equilibrium constant $K_b$ is given by:

$$K_b = \frac{[\text{OH}^- (\text{aq})][\text{CH₃COOH(} \text{aq})]}{[\text{CH₃COO}^- (\text{aq})]} = \frac{x^2}{(0.20 − x)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

so

$$pK_b = 14.00 − 4.76 = 9.24$$

As $pK_b = 4.76$, $K_b = 10^{-4.76}$. Again, $K_b$ is very small, $0.20 − x \sim 0.20$ and hence:

$$x^2 = 0.20 \times 10^{-9.24} \text{ or } x = 0.000011 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$pOH = −\log_{10}[\text{OH}^-] = −\log_{10}[0.000011] = 5.0$$

Finally, pH + pOH = 14 so

$$\text{pH} = 14.0 − 5.0 = 9.0$$

(c) This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used:

$$\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right)$$

As [acetic acid] = [sodium acetate],

$$\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \log_{10} (1) = 0 \text{ and so}$$

$$\text{pH} = pK_a = 4.76$$

6. (a) As the α-COOH group has the lowest pKₐ value, it is the most acidic.

At pH = 1.81, the α-COOH group is in equilibrium with its conjugate base. The pKₐ values of the imidazole N-H and the α-NH₃⁺ groups are higher than the pH value, both exist predominately in the protonated form at pH = 1.81.
(b) As pH = 6.05 is higher than its pKₐ value, the α-COOH group will exist predominately in its conjugate base form. The pKₐ value for the α-NH₃⁺ group is higher than the pH value so it will exist predominately in its protonated form. The ring N-H group will be in equilibrium with its conjugate base form.

As pH = 9.15 is higher than their pKₐ values, the α-COOH and imidazole N-H groups will exist predominately in their conjugate base forms. The α-NH₃ group is in equilibrium with its conjugate base form.

7. The equilibrium of interest is:

$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(l)$$

where $H_2PO_4^-$ is the acid and $HPO_4^{2-}$ is the base. The Henderson-Hasselbalch equation can be used to calculate the required concentrations of each:
\[
\text{pH} = pK_a + \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) \quad \text{or} \quad \log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = \text{pH} - pK_a
\]

\[
\log_{10} \left( \frac{[\text{base}]}{[\text{acid}]} \right) = (7.40 - 7.20) = 0.20
\]

Hence, \( \frac{[\text{base}]}{[\text{acid}]} = 10^{0.20} \)

Both the acid and base have initial concentrations of 0.10 M so the ratio of the volume of each required is:

\[
\frac{V_{\text{base}}}{V_{\text{acid}}} = 10^{0.20} = 1.6
\]

When the two solutions are added together, their total volume = \( V_{\text{base}} + V_{\text{acid}} = 1.0 \) L.

Hence, \( V_{\text{acid}} = 1.0 - V_{\text{base}} \)

\[
\frac{V_{\text{base}}}{1.0 - V_{\text{acid}}} = 1.6 \quad \text{so} \quad V_{\text{base}} = 0.62 \text{ L and } V_{\text{acid}} = 1.0 - V_{\text{base}} = 0.38 \text{ L}
\]