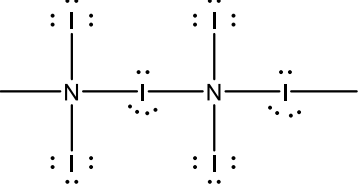
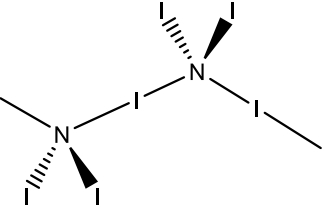


Assessment Schedule – 2017

Scholarship Chemistry (93102)

Evidence Statement

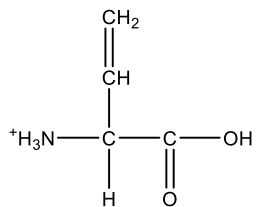
Q	Evidence	Level 3	Scholarship	Outstanding
ONE (a)(i)	<p>Lewis structure: [Total electron count = $6 \times 7 = 42 + 2 \times 5 + 2$ (from adjacent atoms in chain) = 54]</p>  <p>The angle about N is 109°, since tetrahedral electron pair arrangement to minimise repulsion of 4 electron clouds.</p> <p>Angle at I is 180°, since 5 electron pairs will be arranged in a trigonal bipyramid arrangement. With only 2 bonding pairs, a linear arrangement is observed.</p> 	<p>Any of the following:</p> <ul style="list-style-type: none"> Lewis structure and bond angles correct correct reasons for bond angle values correct calculation of $\Delta_r H$ enthalpy, plus entropy discussion interpretation of IR and ^{13}C NMR spectra calculations involving molecular formulae related to mass. 	<p>TWO of the three question parts (a), (b), (c) show understanding of the chemical concepts which are explained / justified.</p> <p><i>(minor error / omission accepted).</i></p>	<p>Bond angles in $\text{NI}_3 \cdot \text{NH}_3$ are correct with accurate and comprehensive justification.</p> <p>AND</p> <p>Discussion of entropy and enthalpy are correct and related to the enthalpies of formation (calculation).</p> <p>AND</p> <p>Compounds Q, R and S are correctly identified with justification.</p> <p>AND</p> <p>Compounds A to F are all identified, with justification.</p>
(ii)	<p>Reaction is $2\text{NI}_3 \cdot \text{NH}_3(s) \rightarrow 2\text{NH}_3(g) + \text{N}_2(g) + 3\text{I}_2(g)$</p> $\Delta_r H = \sum \Delta_f H_{\text{products}} - \sum \Delta_f H_{\text{reactants}}$ $= (3 \times 62 + 2 \times -46) - (2 \times 146) \text{ kJ mol}^{-1}$ $= -198 \text{ kJ mol}^{-1}$ <p>The negative value indicates an exothermic reaction which will be spontaneous.</p> <p>Since the reaction is exothermic, the entropy change of the surroundings is positive.</p> <p>Entropy change to the system is also positive because the solid reactant ($\text{NI}_3 \cdot \text{NH}_3$) forms gaseous products, (N_2, I_2, and NH_3) with more possibility of random motion. Thus, the overall entropy change is positive, and the reaction is spontaneous.</p> <p>In terms of bonds broken and formed – the formation $\text{N} \equiv \text{N}$ releases a large amount of energy and hence forms a very stable product.</p>			<p><i>(ONE aspect of the discussion / justification can lack clarity, OR there is an error in the calculation or interpretation of data).</i></p>

(b)	<p>All compounds have 4 carbons. Structures (1) and (7) are symmetrical, so have 2 carbon environments.</p> <p>Compound R ^{13}C NMR spectrum has 2 peaks. So, R could be (1) or (7). However, (7) is an acid, so it would be expected that in the ^{13}C spectrum, one of the carbon peaks would be found downfield (about 180 ppm), but this is not the case. The peak around 60 ppm is most likely to be from the C–OH group. In the IR, there is a strong –OH stretch at 3600 cm^{-1}, but no peak at 1700 cm^{-1}, which would be present for the C=O stretch. So, Compound R = (1) – 1,4-butanediol.</p> <p>In the ^{13}C NMR spectra for Compounds Q and S, there are 4 peaks, indicating 4 different carbon environments. This matches structures (2) to (6).</p> <p>In the ^{13}C NMR spectra for Compound S, there is a downfield peak around 180 ppm, suggesting an acid or ester functional group is present. In the IR spectrum of Compound S there is no evidence of –OH (no peaks at 3400 cm^{-1}) but there is a peak at 1700 cm^{-1} typical of a C=O for an ester.</p> <p>So, Compound S = (3) – 4-butyrolactone.</p> <p>In the ^{13}C NMR spectra for Compound Q there is one downfield peak around 200 ppm suggesting an aldehyde or ketone functional group is present. There is an aldehyde in structures (2) and (6) but there is no evidence of an acid group in the ^{13}C NMR spectrum (no second downfield peak at 180 ppm).</p> <p>So, Compound Q = (2) – 4-hydroxybutanal.</p>			
(c)	<p>A: Total loss of 14.4% – equivalent to 2 water molecules – $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$</p> <p>B: Total loss of 28.9% – equivalent to 4 water molecules – $\text{CuSO}_4 \cdot \text{H}_2\text{O}$</p> <p>C: Total loss is 36% – equivalent to 5 water molecules – CuSO_4</p> <p>E: 32% of original remains – i.e. mass (M) of 80 which is equivalent to CuO</p> <p>So, D has equivalent amounts of C and E, i.e. CuSO_4 and CuO, i.e. Cu_2SO_5 ($\text{CuS}_{1/2}\text{O}_{2 1/2}$). This corresponds to a mass loss of 52%.</p> <p>At F: total loss is 71% – a further 3% from E. Colour of compound suggests Cu_2O</p> <p>Difference in mass between CuO and $0.5 \times \text{Cu}_2\text{O} = 80 - 0.5(2 \times 63.5 + 16)$ $= 80 - 71.5 = 8.5$</p> <p>% loss of original mass = $\frac{100 \times 8.5}{250} = 3.4\%$</p> <p>OR</p> <p>Mass difference between E and F is about 3% of 250 = 7.5.</p> <p>Suggests 0.5 mol of O lost so empirical formula = $\text{CuO}_{0.5} = \text{Cu}_2\text{O}$.</p>			

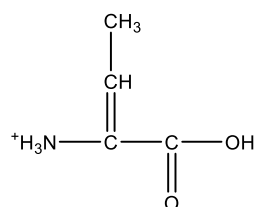
Q	Evidence	Level 3	Scholarship	Outstanding
TWO (a)	<p>Water is a polar solvent and 1,4-dioxane is non-polar.</p> <p>The equilibrium constant $K = \frac{[\text{zwitterion}]}{[\text{uncharged molecule}]}$</p> <p>The lower equilibrium constant for 1,4-dioxane as a solvent is because the zwitterion is charged and less stable in 1,4-dioxane than in water. K_c is lower because, for a given amount of amino acid, less will be present in the zwitterion form.</p> <p>In a non-polar solvent the attraction to the ions will be less favourable so a greater proportion of the uncharged form is present.</p> <p>Amino acids are more soluble in water than in 1,4-dioxane, as in the water, the ionic attractions between the ions in the solid amino acid are replaced by strong attractions between polar water molecules and the zwitterions.</p> <p>In non-polar solvents such as 1,4-dioxane, amino acids are less soluble because of the lesser attractive forces between solvent molecules and the zwitterions. Substances do not dissolve if the solute-solvent attractive forces are much weaker than the solute-solute attractive forces.</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> • discussion of solubility in polar / non-polar solvents • shift in equilibrium related to reactants and products • identification of amino acids linked to data • functional group reactivity • steps in an organic reaction scheme. 	<p>TWO of the three question parts (a), (b), (c) show understanding of the chemical concepts which are explained / justified.</p> <p><i>(minor error / omission accepted).</i></p>	<p>Comprehensive discussion of the effect of the solvent on the equilibrium constant.</p> <p>AND</p> <p>Compounds A to G are correctly identified, with justification.</p> <p>AND</p> <p>Correct reaction scheme, including the final product.</p> <p><i>(ONE aspect of the discussion / justification can lack clarity, OR there is an error in the calculation or interpretation of data).</i></p>

(b) **Compound A = glycine** – the only amino acid that is not chiral (does not form enantiomers) as it does not have a chiral carbon. Also, this is only a two-carbon amino acid (*see total number of C atoms in the tetrapeptide*).

Compound B = threonine as it must have a secondary alcohol to produce two elimination products with concentrated sulfuric acid. The elimination products are:



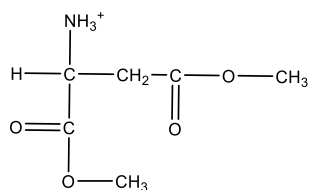
Compound E



Compound F

Compound C = aspartic acid (aspartate) – reacts with $3 \times \text{OH}^-$ per molecule so there are 3 protonated groups on the amino acid ($-\text{COOH}$ and $-\text{NH}_3^+$ and 1 other). When reacted with methanol both the acid groups can form esters adding $2 \times -\text{CH}_3$ to the formula and removing $2 \times \text{H}$ to give $\text{C}_6\text{H}_{12}\text{O}_4\text{N}^+$ (aspartic acid is $\text{C}_4\text{H}_6\text{O}_4\text{N}^+$ in acidic conditions).

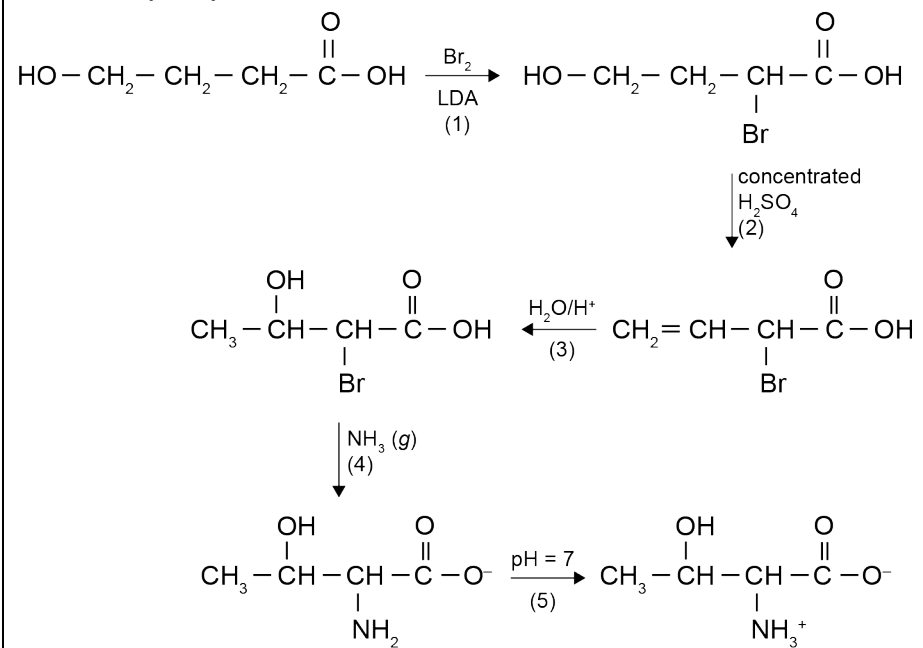
Compound G is:



Compound D = isoleucine – both leucine and isoleucine have molar mass of 131 (constitutional isomers) but isoleucine has 6 distinct peaks in ^{13}C NMR and leucine has only 5.

(c)

4-hydroxybutanoic acid to threonine



(2) could occur before (1).

Q	Evidence	Level 3	Scholarship	Outstanding
THREE (a)	<p>Al(OH)₃: $\text{Al(OH)}_3(s) \rightleftharpoons \text{Al}^{3+}(aq) + 3\text{OH}^-(aq)$ $[\text{Al}^{3+}][\text{OH}^-]^3 = 1.90 \times 10^{-33}$ pH for precipitation: $[\text{OH}^-]^3 = 1.90 \times 10^{-33} / 0.0099$ $[\text{OH}^-] = 5.77 \times 10^{-11}$ i.e. pH = 3.76</p> <p>Ca(OH)₂: $\text{Ca(OH)}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$ $[\text{Ca}^{2+}][\text{OH}^-]^2 = 5.50 \times 10^{-6}$ pH for precipitation: $[\text{OH}^-]^2 = 5.50 \times 10^{-6} / 0.021$ $[\text{OH}^-] = 0.016$ i.e. pH = 12.2</p> <p>Fe(OH)₃: $\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq)$ $[\text{Fe}^{3+}][\text{OH}^-]^3 = 6.00 \times 10^{-38}$ pH for precipitation: $[\text{OH}^-]^3 = 6.00 \times 10^{-38} / 0.010$ $[\text{OH}^-] = 1.82 \times 10^{-12}$ i.e. pH = 2.26</p> <p>So Fe^{3+} will precipitate if the pH is increased to 2.26 by adding NaOH to the solution.</p> <p>Al^{3+} will precipitate when the pH is increased to 3.76.</p> <p>Ca^{2+} will precipitate when the pH is increased to 12.2.</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> • discussion of oxidation-reduction in terms of electron transfer • balanced redox equations • spontaneity linked to E^0 stoichiometric calculations • K_s calculations • pH calculations. 	<p>Shows understanding of oxidation-reduction reactions, but aspects of the discussion lack clarity</p> <p>AND</p> <p>ONE of part (a)(ii) or (b)(i) and (b)(ii) show understanding of the chemical calculations required, but there is a minor error.</p>	<p>Discussion of oxidation-reduction processes includes correctly balanced equations.</p> <p>AND</p> <p>Links the addition of methanol to the redox potential of the materials in the wastewater (which includes electron transfer and the correct mass of Ca(OH)_2 calculation).</p> <p>AND</p> <p>Show, by calculation, how changing the pH can separate out three cations.</p> <p><i>(ONE aspect of the discussion / justification can lack clarity, OR there is an error in the calculation or interpretation of data).</i></p>

<p>(b)(i)</p>	<p>Nitrification: $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \quad E^\circ = 1.23 - 0.88 = \mathbf{0.35 \text{ V}}$ Reaction is spontaneous in standard conditions since E° of the reaction is positive. Electron transfer is from the ammonium ions to oxygen molecules.</p> <p>Denitrification: $2\text{NO}_3^- + 12\text{H}^+ + 10\text{e}^- \rightarrow \text{N}_2 + 6\text{H}_2\text{O} \quad E^\circ = 1.25 \text{ V}$ For reduction to occur a reductant with $E^\circ < 1.25$ must be available and acidic conditions.</p> <p>Methanol needs to be used when the substrate present does not have a low enough reduction potential for a spontaneous transfer of the electrons to the nitrate ions, or if there is insufficient oxidisable material. When methanol is present a spontaneous reaction occurs and methanol loses electrons being oxidised to carbon dioxide.</p> <p>Reaction equation for methanol and nitrate is: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$ $6\text{NO}_3^- + 6\text{H}^+ + 5\text{CH}_3\text{OH} \rightarrow 5\text{CO}_2 + 13\text{H}_2\text{O} + 3\text{N}_2 \quad E^\circ = 1.25 - 0.23 \text{ V} = \mathbf{1.02 \text{ V}}$</p>			
<p>(ii)</p>	<p>Per day: $m(\text{NH}_4^+) = 1.5 \times 10^7 \text{ L} \times 25 \times 10^{-3} \text{ g L}^{-1} = 3.75 \times 10^5 \text{ g}$</p> <p>During the nitrification process, $n(\text{NH}_4^+)$ produces $2n(\text{H}^+)$. $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$</p> <p>For neutralisation, $\text{Ca}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + 2\text{H}_2\text{O}$ $n(\text{NH}_4^+) = n(\text{Ca}(\text{OH})_2)$ $n(\text{NH}_4^+) = \frac{3.75 \times 10^5 \text{ g}}{18.0 \text{ g mol}^{-1}} = 2.083 \times 10^4 = n(\text{Ca}(\text{OH})_2)$</p> <p>$m(\text{Ca}(\text{OH})_2) = n \times M = 2.083 \times 10^4 \text{ mol} \times 74.09 \text{ g mol}^{-1}$ $= 1.543 \times 10^6 \text{ g per day} = 1543 \text{ kg per day}$</p> <p>Per hour: $\frac{1543 \text{ kg}}{24 \text{ hours}} = 64.3 \text{ kg hr}^{-1}$</p>			

Q	Evidence	Level 3	Scholarship	Outstanding
FOUR (a)	<p>Standard solution:</p> $n(\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}) = \frac{10.30 \text{ g}}{392.2 \text{ g mol}^{-1}} = 0.0262621 \text{ mol}$ $n(\text{Fe}^{2+}) = n(\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O})$ $c(\text{Fe}^{2+}) = \frac{0.0262621 \text{ mol}}{0.2500 \text{ L}} = 0.105048 \text{ mol L}^{-1}$ <p>Starting dichromate solution:</p> $n(\text{Fe}^{2+}) = 0.1050 \text{ mol L}^{-1} \times 0.02500 \text{ L} = 0.002626 \text{ mol}$ <p>For the first balanced equation: $(6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \dots)$</p> $n(\text{Cr}_2\text{O}_7^{2-}) = \frac{1}{6} n(\text{Fe}^{2+}) = \frac{1}{6} \times 0.002626 = 0.0004377 \text{ mol}$ $c(\text{Cr}_2\text{O}_7^{2-}) = \frac{0.0004377 \text{ mol}}{0.01743 \text{ L}} = 0.0251120 \text{ mol L}^{-1}$ <p>Wine-dichromate mixture (after reaction)</p> $n(\text{Fe}^{2+}) = 0.1050 \text{ mol L}^{-1} \times 0.01000 \text{ L} = 0.001050 \text{ mol}$ <p>For the first balanced equation: $(6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} \dots)$</p> $n(\text{Cr}_2\text{O}_7^{2-}) = \frac{1}{6} n(\text{Fe}^{2+}) = \frac{1}{6} \times 0.001050 \text{ mol} = 1.751 \times 10^{-4} \text{ mol}$ $c(\text{Cr}_2\text{O}_7^{2-}) = \frac{1.751 \times 10^{-4} \text{ mol}}{0.01988 \text{ L}} = 0.008810 \text{ mol L}^{-1}$ <p>Ethanol concentration</p> $n(\text{Cr}_2\text{O}_7^{2-}) \text{ initial} = 0.02511 \text{ mol L}^{-1} \times 0.1000 \text{ L} = 0.002511 \text{ mol}$ $n(\text{Cr}_2\text{O}_7^{2-}) \text{ end} = 0.008810 \text{ mol L}^{-1} \times 0.126 \text{ L} = 0.001110 \text{ mol}$ $n(\text{Cr}_2\text{O}_7^{2-}) \text{ reacted} = 0.002511 \text{ mol} - 0.001110 \text{ mol} = 0.001401 \text{ mol}$ <p>For the second balanced equation: $(2\text{Cr}_2\text{O}_7^{2-} + 3\text{CH}_3\text{CH}_2\text{OH} + \dots)$</p> $n(\text{CH}_3\text{CH}_2\text{OH}) \text{ in 1 mL wine} = \frac{3}{2} \times n(\text{Cr}_2\text{O}_7^{2-}) = \frac{3}{2} \times 0.001401 \text{ mol} = 0.002102 \text{ mol}$ $m(\text{CH}_3\text{CH}_2\text{OH}) \text{ in 100 mL wine} = 0.002102 \text{ mol} \times 46.07 \text{ g mol}^{-1} = 0.09684 \text{ g}$ $V(\text{CH}_3\text{CH}_2\text{OH}) \text{ in 100 mL wine} = 0.09684 \text{ g} / 0.7893 = 0.1227 \text{ mL}$ <p>Concentration: $0.1227 / 1 \times 100 = \mathbf{12.27\%}$</p> <p>Label states 13.5%. Accepted limits +/- 1.5% so this is within the limits.</p>	<p>Any of the following:</p> <ul style="list-style-type: none"> • concentration calculation for standard solutions • titration calculations • pH calculation (of the weak acid) • relationship between pK_a and $[\text{H}_3\text{O}^+]$. 	<p>Process used for the back-titration analysis of the concentration of ethanol, is mostly correct.</p> <p>AND</p> <p>Most of either part (b)(i) or (b)(ii) correct.</p>	<p>Calculation for the wine analysis compares the wine sample to the guideline.</p> <p>AND</p> <p>Correct concentration of the sulfuric acid.</p> <p>AND</p> <p>There is a correct discussion of the significance of the two pK_a values.</p>

<p>(b)(i)</p>	<p> $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$ $K_a(\text{CH}_3\text{COOH}) = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$ $[\text{CH}_3\text{COOH}] = 0.05 \text{ mol L}^{-1}$ <p>pH of original solution: $\text{pH} = \frac{1}{2}(4.75 - \log(0.1)) = 2.88$ In mixture $\text{pH} = 2.88 - 0.30$ $= 2.58$ so $[\text{H}_3\text{O}^+] = 10^{-2.58}$ $= 2.63 \times 10^{-3} \text{ mol L}^{-1}$</p> $[\text{H}_3\text{O}^+]_{\text{total}} = 2.63 \times 10^{-3} \text{ mol L}^{-1}$ $10^{-4.76} = \frac{[\text{CH}_3\text{COO}^-] \times 10^{-2.58}}{0.05}$ $[\text{CH}_3\text{COO}^-] = 3.30 \times 10^{-4} \text{ mol L}^{-1}$ $[\text{H}_3\text{O}^+]_{\text{total}} = [\text{H}_3\text{O}^+]_{\text{dissociation}} + [\text{H}_3\text{O}^+]_{\text{added}}$ $= [\text{CH}_3\text{COO}^-] + [\text{H}_3\text{O}^+]_{\text{added}}$ $[\text{H}_3\text{O}^+]_{\text{added}} = [\text{H}_3\text{O}^+]_{\text{total}} - [\text{CH}_3\text{COO}^-]$ $= 2.63 \times 10^{-3} \text{ mol L}^{-1} - 3.30 \times 10^{-4} \text{ mol L}^{-1}$ $= 0.00230 \text{ mol L}^{-1} \text{ (diluted solution)}$ <p>So, the concentration of H_2SO_4 in diluted solution is $0.001150 \text{ mol L}^{-1}$ Original concentration of $\text{H}_2\text{SO}_4 = 0.00230 \text{ mol L}^{-1}$</p> </p>			
<p>(ii)</p>	<p>Since $\text{p}K_{a,1}$ is small (negative), this implies that the K_a is large, so the first dissociation reaction lies a long way to the right, and it can be assumed that there is very little H_2SO_4 left in the solution.</p> $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^- + \text{H}_3\text{O}^+$ <p>However, since $\text{p}K_{a,2} = 1.99$, $K_a = 10^{-1.99} = 0.010$. This implies that the second dissociation reaction does not go to completion.</p> $\text{HSO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_3\text{O}^+$ <p>Hence it cannot be assumed that the actual $[\text{H}_3\text{O}^+]$ in a solution of H_2SO_4 is equal to twice $[\text{H}_2\text{SO}_4]$. It will be less than to when the position of the equilibrium in the second reaction is considered.</p> <p>This means that the estimated concentration is low.</p>			