Name	Student Code

32nd IChO • Problem 4 — 10 points

A naturally occurring compound

A naturally occurring compound **A** containing only C, H and O has the following elemental composition, percentage mass,

C: 63.2 %, H: 5.3%, O: 31.5%.

4-1 Derive the empirical formula of compound **A**.

$C_8H_8O_3$

1 mark

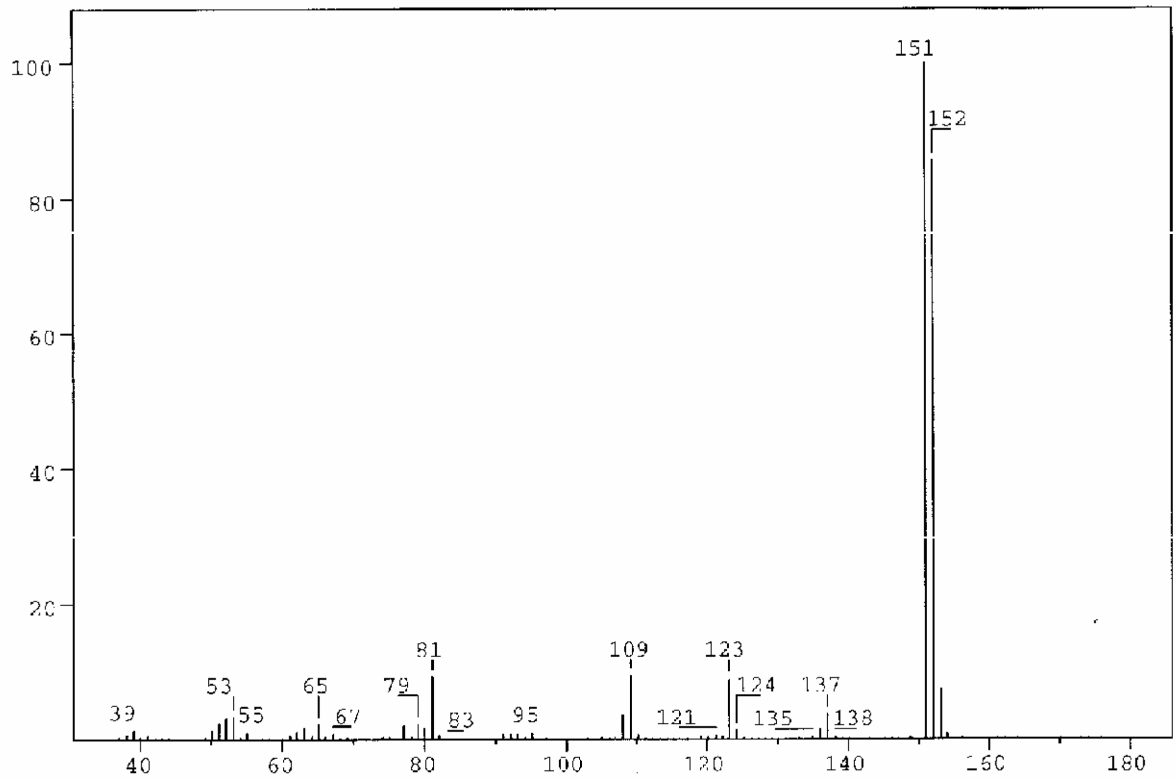


Figure 1

The mass spectrum of compound **A** is shown in Figure 1.

4-2 What is the molecular formula for compound **A**?

$C_8H_8O_3$

1 mark

A solution of **A** in ether is shaken with an aqueous solution of NaOH. After this, no **A** remains in the ether phase.

Another solution of **A** in ether is shaken with an aqueous solution of $NaHCO_3$. **A** remains in the ether phase.

4-3 Which of the following classes of compounds does **A** belong to according to these experiments? Mark with an X.

alcohol ☐	phenol ☒	aldehyde ☐	ketone ☐
acid ☐	ester ☐	ether ☐	

1 mark

Compound **A** gave rise to formation of a silver mirror with Tollens' reagent ($Ag(NH_3)_2^+$).

4-4 Which of the following functional groups does this indicate the presence of in **A**?
Mark with an X.

hydroxy group of an alcohol ☐	hydroxy group of a phenol ☐
carbonyl group of an aldehyde ☒	carbonyl group of a ketone ☐
carboxylic group ☐	ester group ☐
alkoxy group of an ether ☐	

1 mark

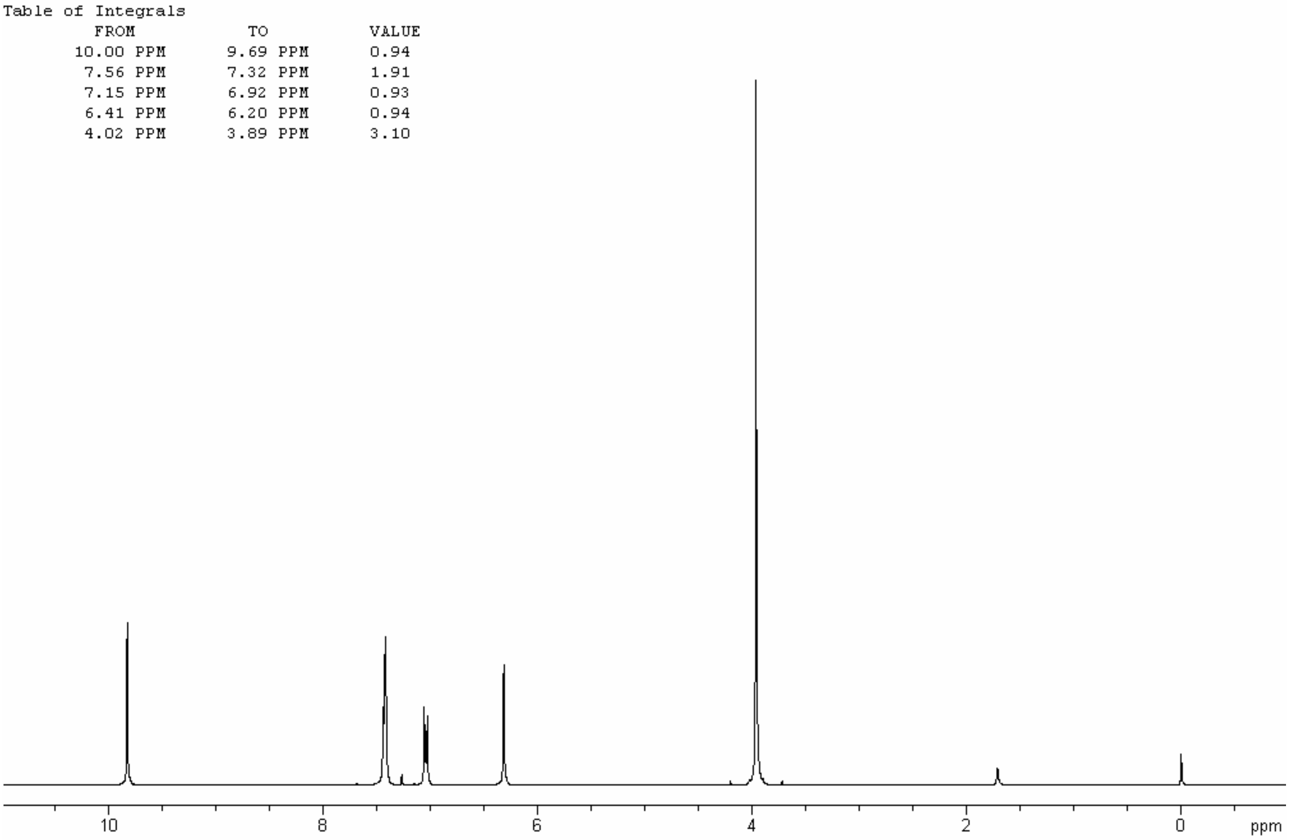


Figure 2a

The ^{1}H NMR spectrum of compound **A** recorded at 300 MHz is shown in Figure 2a (solvent $CDCl_3$ (7.27 ppm), reference tetramethylsilane). The signals at 3.9, 6.3 and 9.8 ppm are singlets. Figure 2b is an expansion of the region 6.9 –7.6 ppm.

Selected chemical shift and coupling constant values are given in Table 1.

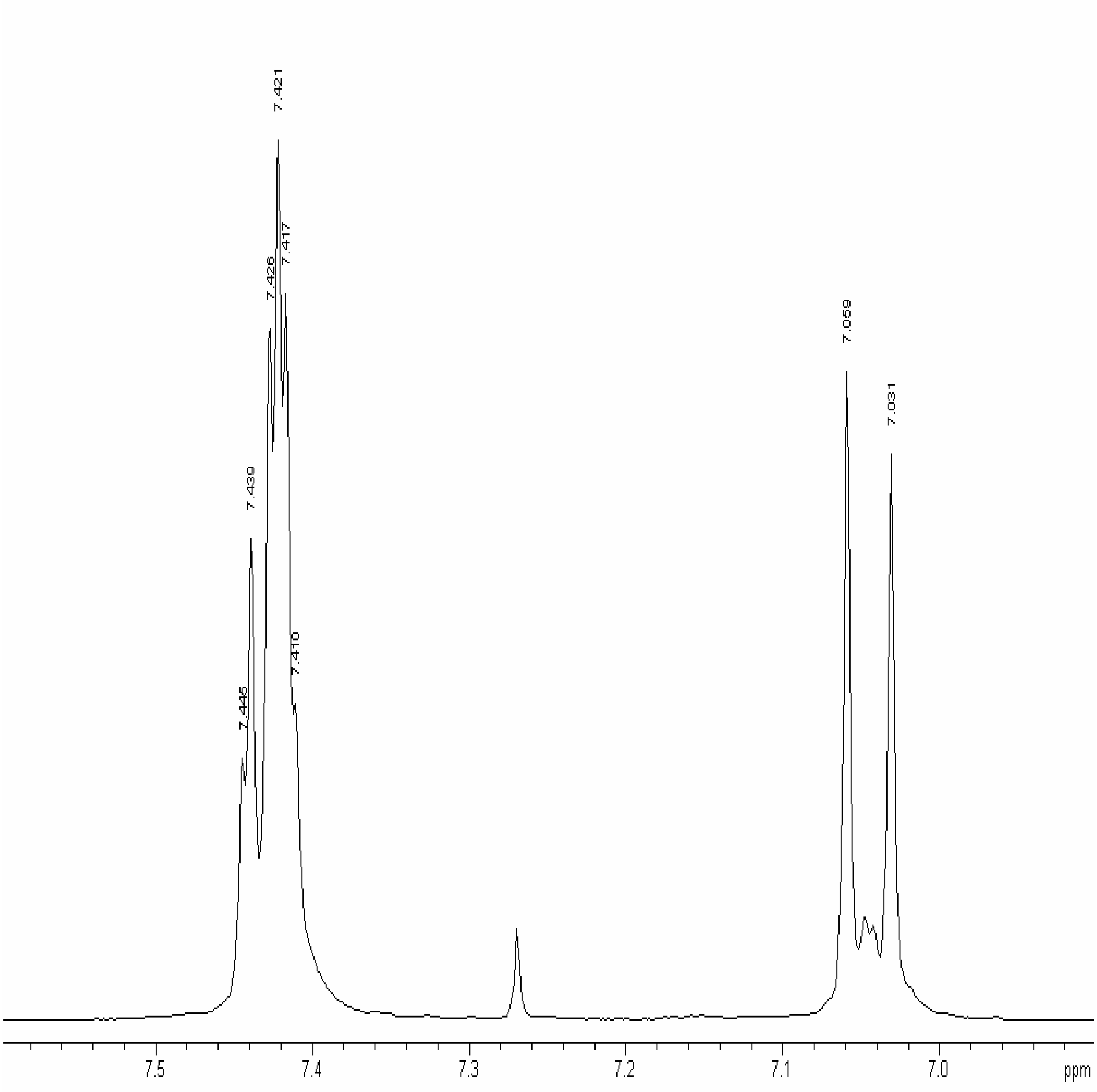


Figure 2b

The signal at 6.3 ppm disappears when a drop of D_2O is added.

4-5 Which of the following does this indicate? Mark with an X.

Exchange of carbon-bonded hydrogen	☐
Exchange of oxygen-bonded hydrogen	☒
Dilution effect	☐
Hydrolysis	☐

1 mark

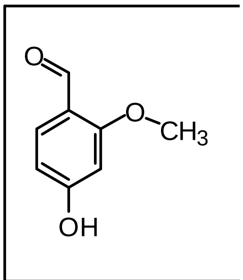
The same signal moves to a lower ppm value upon dilution with $CDCl_3$.

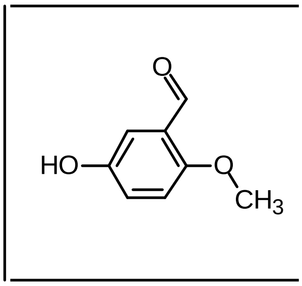
4-6 Which of the following does this indicate?
Indicate the true statements (more than one).

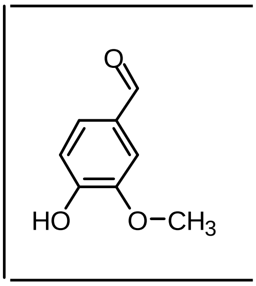
Increased hydrogen bonding	☐
Decrease in hydrogen bonding	☒
Intermolecular hydrogen bonding	☒
Intramolecular hydrogen bonding	☐
No hydrogen bonding	☐

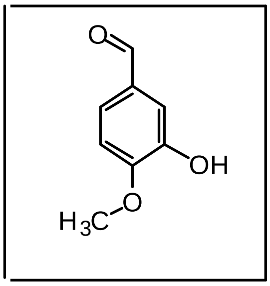
2 marks

4-7 Draw the four possible structural formulas for compound **A** based on the information given above









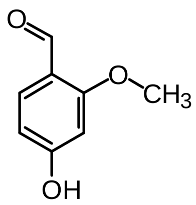
4 mark

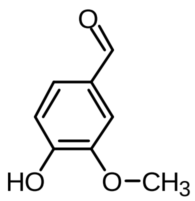
4-8 Give structural formulas for the fragments lost corresponding to the peaks at 137 and 123 mass units in the mass spectrum.

CH_3	HC=O

1 mark

4-9 Two of the isomers have a lower pK_a value than the others. Write the formulas for those.





1 mark

Table 1

^{1}H Chemical Shift δ

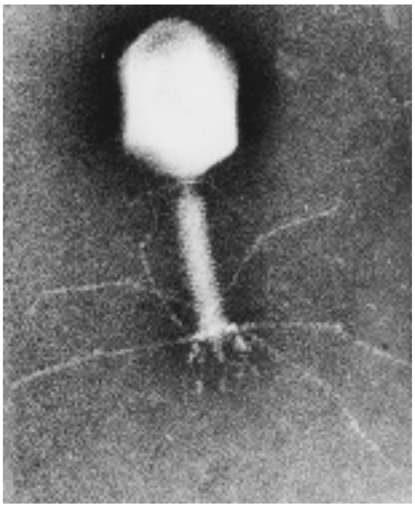
Hydrogens attached to carbon		
Methyl	CH_3–C– CH_3–C=O– CH_3–O–R CH_3–OCOR	0.9 – 1.6 ppm 2.0 – 2.4 ppm 3.3 – 3.8 ppm 3.7 – 4.0 ppm
Methylene	CH_2–C– CH_2–C=O– CH_2–OR CH_2–OCOR	1.4 – 2.7 ppm 2.2 – 2.9 ppm 3.4 – 4.1 ppm 4.3 – 4.4 ppm
Methine	CH–	1.5 – 5.0 ppm depending on the substituents. Generally higher than for methyl and methylene
Alkene		4.0 - 7.3 ppm depending on the substituent
Hydrogens attached to oxygen		
Alcohols	ROH	0.5 -5.0 ppm
Phenols	ArOH	4.0 - 7.0 ppm
Carboxylic acids	RCOOH	10.0 - 13.0 ppm

Selected spin-spin coupling constants

Alkanes (free rotation)	H-C-C-H vicinal	6 - 8 Hz
Alkenes	trans cis geminal	11 - 18 Hz 6 - 12 Hz 0 - 3 Hz
Aromates	ortho meta para	6 - 10 Hz 1 – 4 Hz 0 – 2 Hz

Name	Student Code

Protein and DNA



DNA is composed of 2'-deoxy-nucleotides carrying the bases adenine (A), guanine (G), cytosine (C) and thymine (T). The molar mass of the 2'-deoxy-nucleotide-5'-triphosphates is given in table 2:

Table 2 **dNTP**	**Molar mass /g mol^{-1}**
dATP	487
dGTP	503
dCTP	464
dTTP	478

5-1 Calculate the molar mass of a double stranded DNA fragment consisting of 1000 base pairs with a uniform distribution of the four bases.

dNTP average mass = 483 g mol^{-1}; $M(HP_2O_7^{2-})$ = 175 g mol^{-1};

1000 bp double stranded DNA

M(DNA) = ((483-175) · 2 · 1000 + 2 · 17) g mol^{-1}

= 616034 g mol^{-1}

2 marks

This DNA fragment can be isolated and cloned by using the PCR method (polymerase chain reaction), in which a heat stable DNA polymerase enzyme multiplies the number of molecules of a specific piece of DNA in a cyclic process. Under optimal conditions the number of double-stranded DNA copies doubles in each cycle.

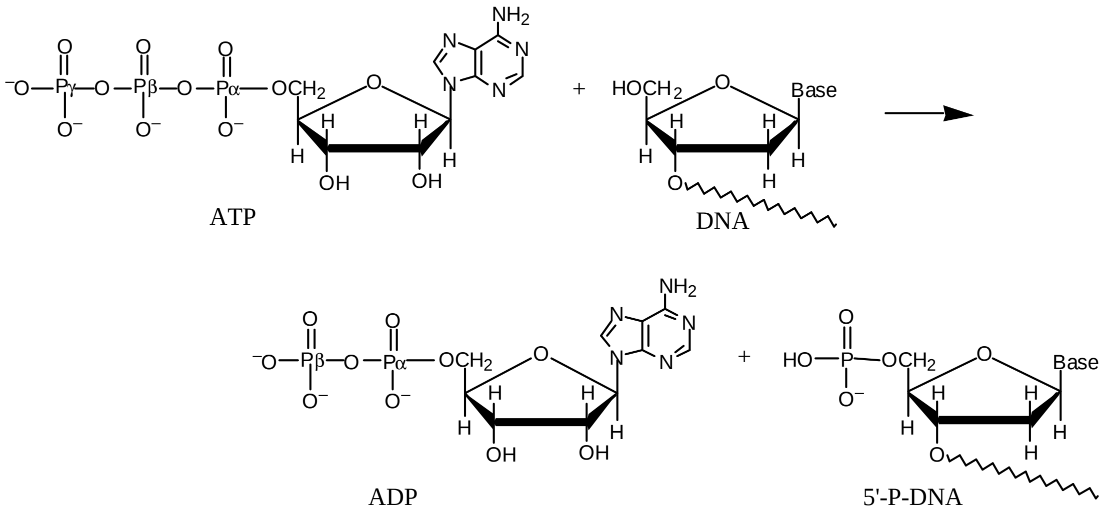
Using the PCR method you perform 30 cycles starting from a single double stranded DNA molecule.

5-2 Calculate the approximate mass of the DNA you obtain from this experiment.

2^{30} copies = 1073741824 copies
Total mass of DNA: $m(\text{DNA}) = 1073741824/N_A \cdot 616350 \text{ g mol}^{-1} = 1.1 \text{ ng}$

2 marks

The bacteria-virus T4 enzyme - polynucleotide kinase (PNK) catalyzes the transfer of the terminal phosphate of ATP (γ-orthophosphate) to the 5'-hydroxyl termini of ribo- and deoxyribonucleotides:



PNK is commonly used to label DNA at the 5'-end with the radioactive phosphorus isotope ^{32}P using ATP in which the γ-P (the outermost of the phosphorus atoms) is replaced with ^{32}P. The amount of ^{32}P and thus the amount of labelled DNA can be measured.

A 10 µL solution containing double stranded DNA is labelled 100% with [γ-^{32}P]ATP by PNK. 37 days ago, the specific activity of [γ-^{32}P]ATP was 10 Ci/mmol or $370 \cdot 10^9$ Bq/mmol. ^{32}P has a half-life of 14.2 days, and during the decay a β-particle is emitted. Now the labelled DNA emits 40000 β-particles/s.

5-3 Calculate the concentration of the DNA solution.

$A = A_0 e^{-kt}$ and $k = \frac{\ln 2}{t_{1/2}} \Rightarrow A_0 = \frac{40000}{e^{-0.0488 \times 37}}$ dps = 243464 dps

which corresponds to $\frac{243464}{370}$ pmol 5'-^{32}P-DNA = 658 pmol 5'-^{32}P-DNA

Since volumen of the labelled DNA is 10 µL, the concentration of the DNA is thus approx. 66 µM

2 marks

In an experiment in which PNK is incubated with [γ-^{32}P]ATP and single stranded DNA, the reaction can be monitored by isolating labeled DNA and measuring the β-particle emission.

Using this kind of measurements in a 1 mL experimental mixture, a labeling of 9 nmol DNA/min was calculated. PNK has a catalytic rate constant (turnover number) of 0.05 s^{-1} and molar mass of 34620 g mol^{-1}.

5-4 Calculate the concentration (in mg/mL) of PNK in the experimental mixture.

Since 9 nmol DNA is labeled per min and the turnover number is 0.05 s^{-1}, the amount of PNK that catalyses the labeling is:

$$\frac{9 \text{ nmol/min}}{0.05 \text{ s}^{-1} \cdot 60 \text{ s/min}} =$$

3 nmol, which corresponds to 3 nmol · 34620 g mol^{-1} = 0.1 mg

The concentration of the PNK in mg/mL is thus 0.1 mg/mL

2 marks

Aromatic amino acids, tryptophan, tyrosine and phenylalanine absorb UV light of a wavelength between 240 nm and 300 nm.

In a protein containing several aromatic amino acids, the sum of the molar absorptivity per amino acid $\Sigma\varepsilon_{\text{amino acid}}$, is approximately equal to the molar absorptivity, $\varepsilon_{\text{protein}}$, for the protein.

The molar absorptivity, $\varepsilon_{\text{amino acid}}$, at 280 nm for tyrosine, tryptophan and phenylalanine is 1400 M^{-1} cm^{-1}, 5600 M^{-1} cm^{-1} and 5 M^{-1} cm^{-1}, respectively. The absorbance of a 10 µM solution of PNK is 0.644 at 280 nm and with 1.00 cm light path. The amino acid sequence of PNK contains 14 tyrosines and 9 phenylalanines.

5-5 Calculate the number of tryptophan residues in a PNK molecule.

$\varepsilon_{\text{Tryptophan}} = 5600\ \text{M}^{-1}\text{cm}^{-1}$; $\varepsilon_{\text{Tyrosine}} = 1400\ \text{M}^{-1}\text{cm}^{-1}$; $\varepsilon_{\text{phenylalanine}} = 5\ \text{M}^{-1}\ \text{cm}^{-1}$

$$\varepsilon = \frac{A}{c \cdot l} \Rightarrow \varepsilon_{\text{PNK}} = \frac{0.644}{10\,\mu\text{M} \cdot 1.00\,\text{cm}} = 64400\ \text{M}^{-1}\ \text{cm}^{-1}$$

$$\Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{phenylalanine}}) = (14 \cdot 1400 + 9 \cdot 5)\,\text{M}^{-1}\text{cm}^{-1} = 19645\ \text{M}^{-1}\text{cm}^{-1}$$

$$\Sigma\varepsilon_{\text{Tryptophan}} = \varepsilon_{\text{PNK}} - \Sigma(\varepsilon_{\text{Tyrosine}} + \varepsilon_{\text{phenylalanine}}) \Rightarrow$$

$$\Sigma\varepsilon_{\text{Tryptophan}} = (64400 - 19645)\ \text{M}^{-1}\text{cm}^{-1} = 44755\ \text{M}^{-1}\text{cm}^{-1}$$

The number of tryptophan residues in a PNK molecule is thus:

$$\frac{44755\ \text{M}^{-1}\text{cm}^{-1}}{5600\ \text{M}^{-1}\text{cm}^{-1}} = 8 \text{ residues}$$

2 marks

Name	Student Code

32^{nd} IChO • Problem 6 — 12 points

Hard Water

In Denmark the subsoil consists mainly of limestone. In contact with ground water containing carbon dioxide some of the calcium carbonate dissolves as calcium hydrogen carbonate. As a result, such ground water is hard, and when used as tap water the high content of calcium hydrogen carbonate causes problems due to precipitation of calcium carbonate in, for example, kitchen and bathroom environments.

Carbon dioxide, CO_2, is a diprotic acid in aqueous solution. The pK_a-values at 0 °C are:

$CO_2(aq) + H_2O(l) = HCO_3^-(aq) + H^+(aq)$ pK_{a1} = 6.630

$HCO_3^-(aq) = CO_3^{2-}(aq) + H^+(aq)$ pK_{a2} = 10.640

The liquid volume change associated with dissolution of CO_2 may be neglected for all of the following problems. The temperature is to be taken as being 0 °C.

6-1 The total concentration of carbon dioxide in water which is saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar is 0.0752 M. Calculate the volume of carbon dioxide gas which can be dissolved in one litre of water under these conditions.

The gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$

$c(CO_2) = 0.0752$ M $n(CO_2) = 0.0752$ mol

The ideal gas equation: $pV = nRT$

$1.00 \text{ bar} \times V = 0.0752 \text{ mol} \times 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1} \times 273.15 \text{ K}$

$V = 1.71$ L

2 mark

6-2 Calculate the equilibrium concentration of hydrogen ions and the equilibrium concentration of CO_2 in water saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar.

$CO_2(aq) + H_2O(l) \; = \; HCO_3^-(aq) + H^+(aq)$

$[H^+] = [HCO_3^-] = x$ and $[CO_2] + [HCO_3^-] = 0.0752$ M

$$K_a = 10^{-6.63}\ \text{M} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x^2}{0.0752\ \text{M} - x}$$

$[H^+] = 0.000133$ M and $[CO_2] = 0.0751$ M

1 mark

6-3 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium hydrogen carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effects.

$CO_2(aq) + H_2O(l) \; = \; HCO_3^-(aq) + H^+(aq)$

$[CO_2] = 0.0751$ M and $[HCO_3^-] = 0.0100$ M

$$K_a = 10^{-6.63}\ \text{M} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \times 0.0100\ \text{M}}{0.0751\ \text{M}}$$

$x = [H^+] = 1.76 \times 10^{-6}$ M

1 mark

6-4 Calculate the equilibrium concentration of hydrogen ions in a 0.0100 M aqueous solution of sodium carbonate saturated with carbon dioxide at a carbon dioxide partial pressure of 1.00 bar. Ignore water dissociation effect.

$CO_2(aq) + CO_3^{2-}(aq) + H_2O(l) \rightarrow 2\ HCO_3^-(aq)$ $[HCO_3^-] = 0.0200$ M

$CO_2(aq) + H_2O(l) \; = \; HCO_3^-(aq) + H^+(aq)$

$$K_a = 10^{-6.63}\ \text{M} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{x \times 0.0200\ \text{M}}{0.0751\ \text{M}}$$

$x = [H^+] = 8.8 \times 10^{-7}$ M

2 marks

6-5 The solubility of calcium carbonate in water at 0 °C is 0.0012 g per 100 mL of water. Calculate the concentration of calcium ions in a saturated solution of calcium carbonate in water.

> 0.0012 g $CaCO_3$ in 100 ml of water
>
> 0.0012 g /100.0872 g mol^{-1} = 0.000012 mol $CaCO_3$ in 100 mL of water
>
> $[Ca^{2+}] = 1.2 \times 10^{-4}$ M

1 mark

The hard groundwater in Denmark is formed via contact of water with limestone in the subsoil which reacts with carbon dioxide dissolved in the groundwater according to the equilibrium equation:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) = Ca^{2+}(aq) + 2\ HCO_3^-\ (aq)$$

The equilibrium constant, K, for this reaction is $10^{-4.25}$ M^2 at 0 °C.

6-6 Calculate the concentration of calcium ions in water in equilibrium with calcium carbonate in an atmosphere with a partial pressure of carbon dioxide of 1.00 bar.

$$K = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]} = 10^{-4.25}\ M^2 \quad \text{and} \quad 2\,[Ca^{2+}] = [HCO_3^-]$$

$$\frac{4\,[Ca^{2+}]^3}{0.0751\ M} = 10^{-4.25}\ M^2 \qquad [Ca^{2+}] = 1.02 \times 10^{-2}\ M$$

3 marks

6-7 A 0.0150 M solution of calcium hydroxide is saturated with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the solution by considering the equilibrium equation given above in connection with problem 6-6.

> $c(Ca(OH)_2) = 0.015$ M
>
> $OH^-\ (aq) + CO_2(aq) \rightarrow HCO_3^-\ (aq)$
>
> All hydroxide has been consumed ($K = 10^{7.37}$ M^{-1}).
>
> From problem 6-6 we found that the maximum possible calcium ion concentration is smaller, *i.e.* precipitation of $CaCO_3$
>
> $[Ca^{2+}] = 1.02 \times 10^{-2}$ M

3 marks

6-8 The calcium hydroxide solution referred to in problem 6-7 is diluted to twice the volume with water before saturation with carbon dioxide gas at a partial pressure of 1.00 bar. Calculate the concentration of calcium ions in the resulting solution saturated with CO_2.

> $c(Ca(OH)_2) = 0.0075$ M
> From problem 6-6 we found that the maximum possible calcium ion concentration we can have is 1.02×10^{-2} M, *i.e.* no precipitation
> $[Ca^{2+}] = 0.75 \times 10^{-2}$ M

2 marks

6-9 Calculate the solubility product constant for calcium carbonate from the data given above.

$$K = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]} = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2]} \times \frac{[CO_3^{2-}][H^+]}{[CO_3^{2-}][H^+]} = \frac{K_{sp}K_{a1}}{K_{a2}}$$

$K_{sp} = 10^{-8.26}$ M^2

3 marks

32nd International Chemistry Olympiad

Copenhagen, Thursday, 6 July 2000

Theoretical Examination

- Write your name and student code (posted at your station) in the upper corner of the first pages of all problems and your student code on all other pages of this problem paper.

- You have 5 hours to complete all of the tasks and record your results in the answer boxes, you must stop your work immediately after the STOP command is given. A delay in doing this by 3 minutes will lead to cancellation of the current task and will result in zero points for the task.

- All results must be written in the appropriate boxes on the pages. Anything written elsewhere will not be marked. Do not write anything on the back of your answer sheets. If you need additional sheets or a replacement answer sheet, request it from the supervisor.

- When you have finished the examination, you must put all of your papers into the envelope provided, then you must seal the envelope. Only papers in the sealed envelope will be marked.

- A receipt will be issued for your sealed envelope. Do not leave the examination room until you are directed to do so.

- Use only the pen and calculator provided.

- A copy of the Periodic Table of the Elements (Merck) is provided.

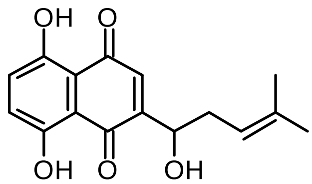
- This examination paper has 29 pages of problems including answer boxes.

- An official English-language version is available only on request.

Name	Student Code

Synthesis of Compounds with Wound Healing Properties

Shikonin is a red compound found in the roots of the plant *Lithospermum erythrorhizon* which grows in Asia. Extracts of the root have been used for centuries in folk medicine and are used today in ointments for healing of wounds.



Shikonin

1-1 How many stereoisomers of Shikonin are possible ?

2

1 mark

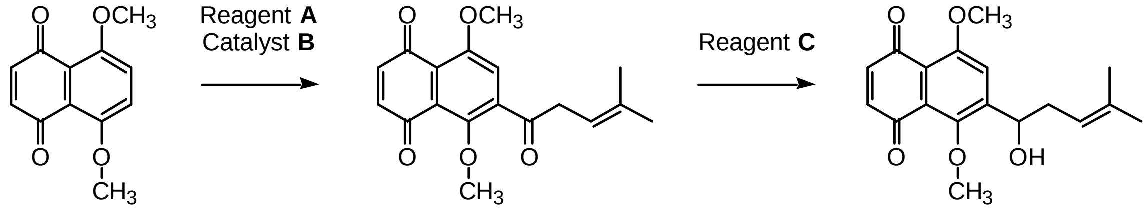
1-2 Do all stereoisomers of Shikonin have the same melting point ?

Mark with an X.

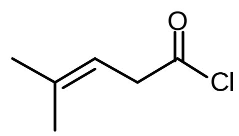
yes	no
X	

1 mark

The following sequence is part of a synthetic route to Shikonin:



1-3 Draw the structural formula of reagent **A**.



2 marks

1-4 Indicate (by means of an X in the appropriate check-box) the correct IUPAC name for reagent **A**.

2-Methyl-2-pentenoyl chloride	☐
1-Chloro-4-methyl-3-pentene	☐
4-Methyl-3-pentenoyl chloride	☒
4-Methyl-3-pentene-1-ol	☐
4,4-Dimethyl-3-butenoyl chloride	☐

1-5 Write the molecular formula of reagent **C**.

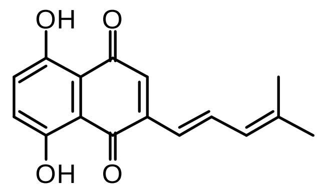
$NaBH_4$
($LiAlH_4$ will be acccepted)

1 mark

Numerous Shikonin analogues have been synthesized with a view to obtaining more potent compounds. One reaction sequence is shown below:

$$\text{Shikonin} \xrightarrow{SOCl_2} \underset{\textbf{D}}{C_{16}H_{15}ClO_4} \xrightarrow[70\ ^\circ C]{\text{KOH in ethanol}} \underset{\textbf{E}}{C_{16}H_{14}O_4}$$

1-6 Draw the structural formula of compound **E**.



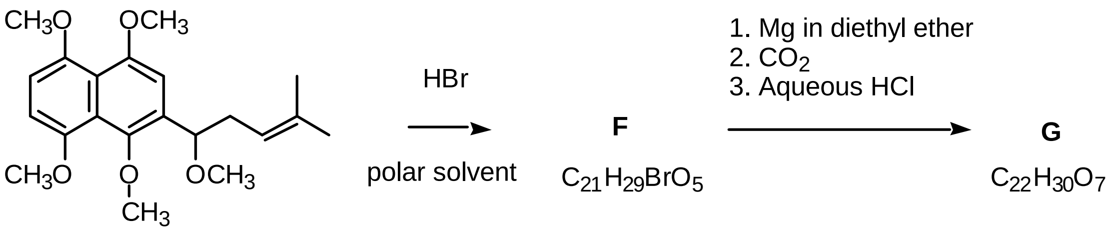
2 marks

1-7 How many stereoisomers of compound **E,** if any, are possible

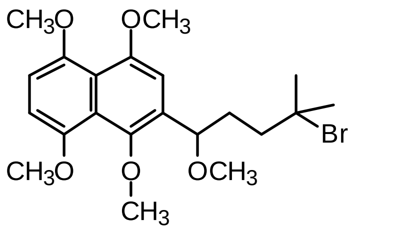
2

1 mark

Another route to useful Shikonin analogues is the following:

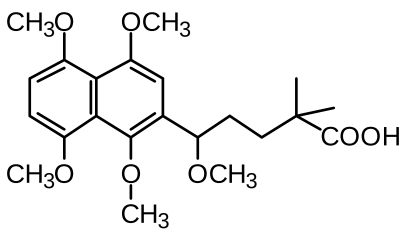


1-8 Draw the structural formula of compound **F**.



2 marks

1-9 Draw the structural formula of compound **G**.



3 marks

Name	Student Code

32nd IChO • Problem 2 — 10 points

Bridge between Denmark and Sweden

On July 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was

officially opened. It consists of a tunnel from Copenhagen to an artificial island, and a bridge from the island to Malmö in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production a small amount of gypsum, $CaSO_4{\cdot}2H_2O$, is added to improve subsequent hardening of the concrete. The use of elevated temperatures during the final production may lead to formation of unwanted hemihydrate, $CaSO_4{\cdot}\frac{1}{2}H_2O$. Consider the following reaction:

$$CaSO_4{\cdot}2H_2O(s) \rightarrow CaSO_4{\cdot}\tfrac{1}{2}H_2O(s) + 1\tfrac{1}{2}H_2O(g)$$

The following thermodynamic data apply at 25 °C, standard pressure: 1.00 bar :

Compound	H ·/(kJ mol^{-1}) (ΔH_f ·)	S ·/(J K^{-1} mol^{-1})
$CaSO_4{\cdot}2H_2O(s)$	–2021.0	194.0
$CaSO_4{\cdot}\frac{1}{2}H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant: R = 8.314 J mol^{-1} K^{-1} = 0.08314 L bar mol^{-1} K^{-1}

0 °C = 273.15 K.

2-1 Calculate ΔH° (in kJ) for transformation of 1.00 kg of $CaSO_4 \cdot 2H_2O(s)$ to $CaSO_4 \cdot ½H_2O(s)$. Is this reaction endothermic or is it exothermic?

$\Delta H^\circ = -1575.0 \text{ kJ mol}^{-1} + 1½\,(-241.8) \text{ kJ mol}^{-1} - (-2021.0 \text{ kJ mol}^{-1})$
$= 83.3 \text{ kJ mol}^{-1}$

$n = m / M = 1000\text{g} / 172.18 \text{ g mol}^{-1} = 5.808 \text{ mol}$

$n\,\Delta H^\circ = \underline{484 \text{ kJ}}$

Mark with an X.: Endothermic ☒ Exothermic ☐

2 marks

2-2 Calculate the equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2H_2O(s)$, $CaSO_4 \cdot ½H_2O(s)$ and $H_2O(g)$ at 25 °C.

$\Delta S^\circ = 130.5 \text{ J K}^{-1} \text{ mol}^{-1} + 3/2 \times 188.6 \text{ J K}^{-1} \text{ mol}^{-1} - 194.0 \text{ J K}^{-1} \text{ mol}^{-1}$
$= 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = 17886 \text{ J mol}^{-1}$

$\Delta G^\circ = -RT \ln K$

$K = (p(H_2O))^{3/2} = 7.35 \times 10^{-4}$ (pressure in bar)

$p(H_2O) = \underline{8.15 \times 10^{-3} \text{ bar}}$

2 marks

2-3 Calculate the temperature at which the water vapour pressure is 1.00 bar in the system described in problem 2-2. Assume that ΔH° and ΔS° are temperature independent.

$p(H_2O)$ = 1.00 bar implies K = 1.00 and $\Delta G^\circ = -RT \ln K = 0$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$0 = 83300 \text{ J K}^{-1} - T \; 219.4 \text{ J K}^{-1} \text{ mol}^{-1}$

T = 380 K or 107 ºC

2 marks

Corrosion of metals is associated with electrochemical reactions. This also applies for the formation of rust on iron surfaces, where the initial electrode reactions usually are:

(1) $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

(2) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

An electrochemical cell in which these electrode reactions take place is constructed. The temperature is 25 ºC. The cell is represented by the following cell diagram:

$Fe(s) \mid Fe^{2+}(aq) \mid\mid OH^-(aq), O_2(g) \mid Pt(s)$

Standard electrode potentials (at 25 ºC):

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $E^\circ = -0.44$ V

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ $E^\circ = 0.40$ V

Nernst factor: $RT \ln 10 / F$ = 0.05916 volt (at 25 ºC)
Faraday constant: F = 96485 C mol^{-1}

2-4 Calculate the standard electromotive force (the standard cell voltage), E°, at 25 ºC.

$E^\circ(\text{cell}) = E^\circ(\text{right}) - E^\circ(\text{left}) = 0.40 \text{ V} - (-0.44 \text{ V}) = 0.84 \text{ V}$

1 mark

2-5 Write down the overall reaction which takes place during discharge of the cell under standard conditions.

oxidation takes place at the negative, left half-cell

left half: $2\ Fe \rightarrow 2\ Fe^{2+} + 4e^-$ (multiplied by 2)

right half: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

overall: $2\ Fe + O_2 + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ OH^-$

1 mark

2-6 Calculate the equilibrium constant at 25 °C for the overall cell reaction.

$K = [Fe^{2+}]^2\ [OH^-]^4 / p(O_2)$ (conc. in M and pressure in bar)

$\Delta G^{\cdot} = -n\ F\ E^{\cdot}(\text{cell}) = -R\ T \ln K$

$K = \underline{6.2\times10^{56}\ (\text{M}^6\ \text{bar}^{-1})}$

2 marks

2-7 The overall reaction referred to above is allowed to proceed for 24 hours under standard conditions and at a constant current of 0.12 A. Calculate the mass of Fe converted to Fe^{2+} after 24 hours. Oxygen and water may be assumed to be present in excess.

$Q = I\ t = 0.12\ \text{A} \times 24 \times 60 \times 60\ \text{s} = 10\ 368\ \text{C}$

$n(e^-) = Q / F = 10\ 368\ \text{C} / (96485\ \text{C mol}^{-1}) = 0.1075\ \text{mol}$

$m(Fe) = n(Fe)\ M(Fe) = 1/2 \times 0.1075\ \text{mol} \times 55.85\ \text{g mol}^{-1} = \underline{3.0\ \text{g}}$

2 marks

2-8 Calculate E for the cell at 25 °C for the following conditions:
$[Fe^{2+}]$ = 0.015 M, $pH_{\text{right-hand half-cell}}$ = 9.00, $p(O_2)$ = 0.700 bar.

$$E(\text{cell}) = E^{\circ}(\text{cell}) - \frac{0.05916\ \text{V}}{n} \log \frac{[Fe^{2+}]^2 [OH^-]^4}{p(O_2)}$$

(conc. in M and pressure in bar)

pH = 9.00 implies $[H^+] = 10^{-9}$ M and $[OH^-] = 10^{-5}$ M

$$E(\text{cell}) = 0.84\ \text{V} - \frac{0.05916\ \text{V}}{4} \log \frac{0.015^2 (10^{-5})^4}{0.700} = \underline{1.19\ \text{V}}$$

2 marks

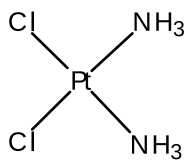
Name	Student Code

32^{nd} IChO • Problem 3 — 9 points

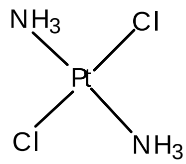
Bioinorganic Chemistry

The square planar complex *cis*-diamminedichloroplatinum(II) is an important drug for the treatment of certain cancers.

3-1 Draw the structures of *cis*- and *trans*-diamminedichloroplatinum(II) and label each structure as *cis* or *trans*.



cis



trans

1 mark

A number of ionic compounds also have the empirical formula $Pt(NH_3)_2Cl_2$.

3-2 Write molecular formulas for all possible ionic compounds which comply with the following conditions: each compound has

1) empirical formula $Pt(NH_3)_2Cl_2$
2) an anion and a cation and is composed of discrete, monomeric square planar platinum(II) complex
3) only one type of cation and one type of anion. The answer must clearly reveal the composition of each discrete platinum(II) complex entity in each compound.

$[Pt(NH_3)_4][PtCl_4]$

$[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]$

$[Pt(NH_3)_3Cl]_2[PtCl_4]$

$[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$

4 marks

3-3 How many 5d electrons does the platinum(II) ion have?

8

1 mark

The valence d-orbital energy splitting diagram for a square planar complex can be regarded as being derived from that for an octahedral complex in which the metal-ligand interactions due to the two ligands coordinated along the *z* axis vanish, while the bonds to the four remaining ligands (coordinated along the *x* and *y* axes) become stronger.

3-4 Which of the five 5d orbitals attain the highest energy (*i.e.* is the least likely to be occupied by electrons) in the general case of a square-planar Pt(II) complex?

$5d_{x^2-y^2}$ In a square planar complex the four ligand atoms fall on the *x* and *y* axes along which this orbital, if filled, would also have electron density concentrated.

2 marks

Serum transferrin (abbreviated: Tf) is a monomeric protein whose main function in the human body is the transport of iron(III). Each transferrin molecule can bind up to two iron(III) ions with stepwise binding constants K_1 and K_2 at biological conditions except that the temperature is 25 °C corresponding to the reactions

$Fe^{III} + Tf \rightleftharpoons (Fe^{III})Tf$ $K_1 = 4.7 \times 10^{20}$ M^{-1}

$Fe^{III} + (Fe^{III})Tf \rightleftharpoons (Fe^{III})_2Tf$ $K_2 = 2.4 \times 10^{19}$ M^{-1}

In the diferric protein, $(Fe^{III})_2Tf$, the two iron(III) ions are bound at two similar, but <u>non-identical</u> sites, and the two possible monoferric protein products, $(Fe^{III})Tf$, can be denoted $\{Fe^{III}\cdot Tf\}$ and $\{Tf\cdot Fe^{III}\}$. Their relative abundance at equilibrium is given by the constant $K = [\{Tf\cdot Fe^{III}\}][\{Fe^{III}\cdot Tf\}]^{-1} = 5.9$.

3-5 Calculate the values of the two constants $K_1' = [\{Fe^{III} \cdot Tf\}][Fe^{III}]^{-1}[Tf]^{-1}$ and $K_1'' = [\{Tf \cdot Fe^{III}\}][Fe^{III}]^{-1}[Tf]^{-1}$, respectively, corresponding to the formation of each monoferric form of transferrin.

The concentration of monoferric forms of transferrin is
$[(Fe^{III})Tf] = [\{Fe^{III} \cdot Tf\}] + [\{Tf \cdot Fe^{III}\}]$

$K_1' + K_1'' = K_1, \qquad K_1'K = K_1''$

$K_1' = \dfrac{K_1}{1+K} = \dfrac{4.7 \times 10^{20}\ \mathrm{M}^{-1}}{1+5.9} =$
$\underline{6.8 \times 10^{19}\ \mathrm{M}^{-1}}$

$K_1'' = K_1 - K_1' =$
$(4.7 - 0.68) \times 10^{20}\ \mathrm{M}^{-1} =$
$\underline{4.0 \times 10^{20}\ \mathrm{M}^{-1}}$

4 marks

3-6 Calculate the values of the two constants $K_2' = [(Fe^{III})_2Tf][Fe^{III}]^{-1}[\{Fe^{III} \cdot Tf\}]^{-1}$ and $K_2'' = [(Fe^{III})_2Tf][Fe^{III}]^{-1}[\{Tf \cdot Fe^{III}\}]^{-1}$ respectively, corresponding to the formation of diferric transferrin from each of the monoferric forms

$K_1'K_2' = K_1''K_2'' = K_1K_2$

$K_2' = \dfrac{K_1K_2}{K_1'} =$

$\dfrac{4.7 \times 10^{20}\ \mathrm{M}^{-1} \times 2.4 \times 10^{19}\ \mathrm{M}^{-1}}{6.8 \times 10^{19}\ \mathrm{M}^{-1}} =$
$\underline{1.7 \times 10^{20}\ \mathrm{M}^{-1}}$

$K_1''K_2'' = K_1K_2$

$K_2'' = \dfrac{K_1K_2}{K_1''} =$

$\dfrac{4.7 \times 10^{20}\ \mathrm{M}^{-1} \times 2.4 \times 10^{19}\ \mathrm{M}^{-1}}{4.0 \times 10^{20}\ \mathrm{M}^{-1}} =$
$\underline{2.8 \times 10^{19}\ \mathrm{M}^{-1}}$

4 marks

The bound iron(III) ion at each binding site is surrounded by six donor atoms from various ligands. Thus, two oxygen atoms of a carbonate anion coordinate to the metal, and the following amino acid side chains from the protein primary structure also coordinate to the iron(III) ion with one potential donor atom each: one aspartate, one histidine and two tyrosine residues.

3-7 What is the total number of oxygen donor atoms that surround a 6-coordinate iron(III) ion in transferrin?

5	(= 2 (CO_3^{2-}) + 1 (Asp(O^-)) + 2 (2 × Tyr(O^-))

2 marks