## AUSTRALIAN CHEMISTRY OLYMPIAD

Please note that this answer book will be photocopied when returned and then split so that answers are sent to the appropriate markers. For this reason it is extremely important that you observe instructions 6 to 7.

Instruction to candidates

(1)   You are allowed **10 minutes** to read this paper, and **3 hours** to complete the questions.

(2)   You are **not** permitted to refer to books, notes or periodic tables but you may use a non programmable electronic calculator and molecular models, molecular models are not considered essential.

(3)   You must attempt **all** questions. All questions are of equal value.

(4)   Appropriate data can be found at the end of questions 3 and 4.

(5)   Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.

(6)   Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.

(7)   Ensure that your name is written in the appropriate place on **each page** of your examination booklet.

(8)   Use **only** **black** or **blue** **ball point pen** for your written answers, **pencil or other coloured pens are not acceptable.**

Question 1
a)   One of the pigments found in carrots is β-carotene. It contains of a conjugated π-system which extends over the length of the molecule.
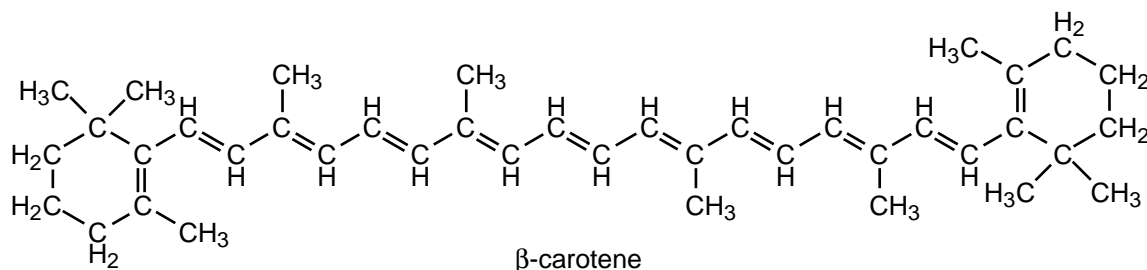
β-carotene

Average C—C bond length in β-carotene is 1.4 Å.

Approximating the system as a "particle in a box", draw a diagram showing the orbital energies and occupancies. Illustrate each orbital as a wave with nodes at each end.

b)   In this model, the energy levels are denoted by a principle quantum number, n = 1, 2, … .The energy of level n is given by the following formula

$$E_n = \frac{n^2 h^2}{8\ mL^2}$$

where h is the Planck constant (6.626×10^{-34} Js), m is the mass of an electron (9.1039×10^{-31} kg) and L is the length of the "box".

Many transitions are possible, within the constraints of the Pauli Exclusion Principle. Which of these transitions are in the visible region? Estimate the colour of carrots **based on your calculations**.

wavelength (nm)	colour
600	reddish brown
590	orange
580	yellow
555	greenish yellow
530	green
500	greenish blue
480	blue
430	bluish violet
400	violet

Question 2

The noble gases were once thought to be completely inert and incapable of chemical bond formation. It is now known that this is not the case, and most general chemistry textbooks now describe some of the krypton- and xenon-containing compounds which have been isolated.

a)   Using valence-bond theory, predict the geometries possible for XeF_2 and XeF_4.

b)   What is the oxidation number of Xe in each of these compounds? Would you expect them to behave as oxidizing or as reducing agents?

c)   Helium is widely known as the most inert of all the elements; yet even helium's 'inertness' is strictly only applicable to its interactions with other neutral atoms and molecules. Compounds of helium, involving formal chemical bonds between helium and other atoms, can exist when the overall entity bears a (generally positive) charge. For example, the helium atom can form observable (though not necessarily long-lived) compounds with H^+, with He^+, and with He^{2+}. Use MO theory to determine the bond order for each of these cases.

d).   Stable diatomic dications of the formula XHe^{2+} are generally only possible when $IE(X^+) < IE(He)$: that is, when the energy required to further ionize X^+ is less than that needed to ionize He. Without recourse to a table of successive ionization energies, identify which element (called 'Z'), from H to Ar, is most likely to fulfil this criterion.

e)   Which of the immediate neighbours of your identified element Z (ie those elements either 1 left, 1 right, 1 above, or 1 below it in the periodic table) is most likely to also form a stable dication with He? Which of Z's neighbours is least likely to form such a dication?

Question 3

a)   Neutron activation analysis is a technique whereby an unknown sample is irradiated with a high flux of neutrons. The neutrons may be captured by the nuclei present in the sample and convert them into isotopes of the same atomic number, but of higher mass. This usually leaves the nucleus unstable and so radioactive decay of the activated nucleus results. Below is a table showing the rate of disintegrations measured for a binary alloy of unknown composition after being neutron irradiated.

time (hours)	count rate (disintegrations per second)
0	280
5	120
10	74
26	41
53	20
80	10

Given the following half lives for some β-emitting isotopes, determine the *qualitative* composition of the alloy. Explain you reasoning behind your analysis.

Isotope	$t_{1/2}$ (hours)
$^{24}_{11}$Na	15.0
$^{56}_{25}$Mn	2.58
$^{76}_{33}$As	26.5
$^{90}_{39}$Y	64.2
$^{99}_{42}$Mo	66.0

(b)   A hydrogen-oxygen fuel cell is supplied with the two gases at 1 atm pressure and is capable of delivering a steady power of 1 kW at an operating temperature of 298 K. Estimate the approximate power output at 363 K given the same rate of fuel consumption.

[Data: at 298K H_2O: $\Delta G°_f = -237$ kJ mol^{-1}, $\Delta H°_f = -285$ kJ mol^{-1}, $S° = 70$ JK^{-1}mol^{-1}

H_2: $S° = 131$ JK^{-1}mol^{-1}

O_2: $S° = 205$ JK^{-1}mol^{-1}]

Question 4

A sample of effluent water from a chemical plant was collected and analysed for various contaminants.

The first analysis was for iron by redox titration with permanganate. Iron normally exists as a mixture of Fe^{2+} and Fe^{3+}. Before the analysis was carried out, the Fe^{3+} was reduced using Zn and HCl(aq).

a)   Explain why Zn/HCl was used rather than one of the numerous other reducing agents available (eg Sn^{2+}, NO_2^-)?

b)   In the titration, 18.20 mL of 5.013×10^{-3} M $KMnO_4$ were required to reach an end point with 25.00 mL of the effluent solution.
   (i)   Balance the redox equation for the reaction by the method of half-equations.
   (ii)   What is the total concentration of iron-containing species in the effluent solution?
   (iii)   What is $[Fe^{2+}]$ when the end point is reached? (MnO_4^- ions can be seen at concentrations of about 1×10^{-5} M). How quantitative is this titration?

c)   It was then proposed to measure the ratio of Fe^{2+} to Fe^{3+} in the original sample by an electrochemical measurement. This was done, and a reduction potential for the solution was found to be +0.84 V. However, a separate analysis had revealed that the effluent was 2.1×10^{-5} M in F^- ion. Fluoride ion forms the complex $[FeF^{2+}]$ with Fe^{3+} ion.
   (i)   Calculate the concentrations of $[Fe^{2+}]$ in terms of the concentration of free Fe^{3+}.
   (ii)   Calculate $[FeF^{2+}]$ in terms of the concentration of free Fe^{3+}.
   (iii)   Calculate the actual concentration of each iron containing species in the effluent solution.

In a rather cunning move, the chemist in charge of the analysis decided to put the Fe^{3+} in the solution to good use in a titration of Ag^+ content. The plan was to titrate the effluent with SCN^- ion to form AgSCN(s). The end point would be indicated by the formation of the complex $[FeSCN^{2+}]$ which is highly coloured (visible at about 1×10^{-5} M). It was estimated that $[Ag^+]$ in the effluent was between 1×10^{-3} M and 1×10^{-4} M.

d)   Given the concentration of Fe^{3+} that you calculated above, determine whether the titration will be quantitative under these conditions. State any assumption that you have made.

[Data: $E°_{(Fe^{3+}/Fe^{2+})} = +0.77$ V $E°_{(Sn^{4+}/Sn^{2+})} = +0.15$ V $E°_{(NO_3^-/HNO_2)} = 0.94$ V

$E°_{(H^+/H_2)} = +0.0$ V $E°_{(Zn^{2+}/Zn)} = -0.76$ V $E°_{(MnO_4^-/Mn^{2+})} = +1.51$ V

$$K_{sp}(AgSCN) = 1 \times 10^{-12} \qquad K_{stab}([FeSCN^{2+}]) = 1 \times 10^3 \qquad K_{stab}([FeF^{2+}]) = 1 \times 10^5 \quad]$$

Question 5

Ambucaine ($C_{17}H_{28}N_2O_3$) is a local anaesthetic derived from benzoic acid. Its synthesis begins with methyl benzoate, which is nitrated with a mixture of sulfuric and nitric acids, giving **A**. After saponification with sodium hydroxide and neutralisation of the resulting salt, **B** ($C_7H_5NO_4$) is isolated, and is then submitted to reaction with hydrogen in the presence of a palladium catalyst. The reduced product **C** is allowed to react with nitrous acid (or $HCl/NaNO_2$), followed by heating in water, to give **D** ($C_7H_6O_3$). A further nitration of **D** affords **E** (note that steric effects will be determinative here). Heating with **E** in ethanol in the presence of hydrochloric acid gives **F** ($C_9H_9NO_5$). **F** is treated with potassium hydroxide and 1-bromobutane and **G** ($C_{13}H_{17}NO_5$) is isolated. The subsequent saponification of **G** with KOH and reaction with thionyl chloride, and finally with diethylethanolamine affords **H** ($C_{17}H_{26}N_2O_5$). Ambucaine is obtained by catalytic hydrogenation of **H**.
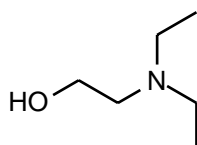
Diethylethanolamine   Methyl benzoate
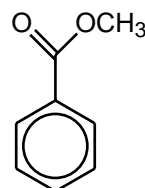
(a)   Depict the reaction path, labelling **A-H** and ambucaine.

(b)   Why is a certain group added in the step converting **E** to **F**, and then subsequently removed again?