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AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL EXAMINATION — PART A

2000

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 8.

<u>**Instructions to candidate**</u>

(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.

(3)   All questions to be attempted. A guide for time allocation is supplied at the beginning of each question.

4)   Data is supplied, where necessary, with each question.

(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 <u>black</u>** or **<u>blue</u> pen** for your written answers, **pencil or other coloured pens are <u>not</u> acceptable.**

Question 1 (45 minutes)

The catalytic decomposition of ammonia into nitrogen and hydrogen was studied at 1100 °C. No nitrogen or hydrogen were initially present, and the following data was obtained:

Half-life (min)	7.6	3.7	1.7
Initial partial pressure of NH_3 (atm)	0.349	0.171	0.076

a)   (i)   Determine the order of reaction.

       (ii)   Determine the rate constant for the reaction.

b)   (i)   Consider an infinitesimal change in internal energy, dU, arising from a combination of reversible heat transfer and reversible work. Assuming the system can only do P-V work, derive an expression for dU solely in terms of the state functions of the system: S, T, P and V.

       (ii)   Now consider a change in Gibbs free energy, dG. Use the definitions of G, H, and your equation obtained in (i) to derive an expression for dG in terms of state functions of the system.

(iii)   Suppose a system is at its liquid-gas phase boundary (i.e. liquid and gaseous phases are in equilibrium), and we make an infinitesimal change in pressure, dP, and an infinitesimal change in temperature, dT, such that the two phases are still in equilibrium. Consider molar quantities, and use your answer to (ii) to obtain an expression for dP/dT, then express dP/dT in terms of $\Delta_{vap}H°$, ΔV_m (change in molar volume), and T_b (boiling point), justifying any assumptions you make.

(iv)   Use the ideal gas law to simplify your answer to (iii) further, and integrate this expression to obtain the following temperature dependence of the vapour pressure of a liquid, stating any assumptions you make:

$$\ln\left(\frac{P_2}{P_1}\right) = -\left(\frac{\Delta_{vap}H°}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

(v)   At the last camp below the summit of Mount Everest, air pressure is around 40.0 kPa. An intrepid explorer decides to cook himself some 2 minute noodles, however after 2 minutes cooking he finds them still rather crunchy. If the noodles take 120 seconds to cook at sea level and normal air pressure (101.3 kPa), for how long should he have cooked them? Answer to the nearest second.

Assume the cooking process obeys 1st order kinetics and has an activation energy of $+70.0 \text{ kJ mol}^{-1}$, and the assumptions in (iii) and (iv) are justified.

Data: $\Delta_{vap}H° (H_2O) = +44.0 \text{ kJ mol}^{-1}$, $R = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$.

Question 2 (45 minutes)

**Data:** $Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$ $pK_{stab} = -2.00$
$Fe^{3+} + F^- \rightleftharpoons FeF^{2+}$ $pK_{stab} = -5.00$
$pK_a (HF) = 3.20$

Part 1   Iron(III) ions form the highly coloured $(FeSCN)^{2+}$ complex with thiocyanate ions in solution. The colour can be detected by the naked eye when $[(FeSCN)^{2+}] \geq 1.0 \times 10^{-5}$ M.

a) 1.0×10^{-3} mol of $FeCl_3$ and 1.0×10^{-2} mol of KSCN are dissolved in 1.0 L of water.

(i)   Calculate the equilibrium concentrations of Fe^{3+}, SCN^- and $(FeSCN)^{2+}$

(ii)   Will the solution be coloured?

b)   Potassium fluoride is added to the solution. F^- ions form a colourless complex with Fe^{3+} ions:

$$Fe^{3+} + F^- \rightleftharpoons (FeF)^{2+}$$
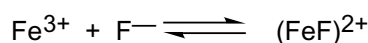
(i)   What quantity of HF must be added to the above $(FeSCN)^{2+}$ solution before the colouring due to $(FeSCN)^{2+}$ disappears? In answering this question, you may neglect the volume change due to the addition of HF.

(ii)   Calculate the ratio $[(FeSCN)^{2+}] / [(FeF)^{2+}]$ and relate this value to the K_{stab} values for the complex ions and the concentrations of thiocyanate and fluoride ions in solution.

c)   As you know, HF is a weak acid, whereas HSCN is a strong acid. A strong acid (consider this simply as a source of H^+ ions) is added to a solution containing 1.0×10^{-3} M $FeCl_3$, 0.10 M KSCN and 0.10 M KF. At what pH value will the $(FeSCN)^{2+}$ colouring appear? (Neglect any volume changes due to the addition of the strong acid).

Part 2   Consider the apparatus shown:

        Solution 1   Solution 2
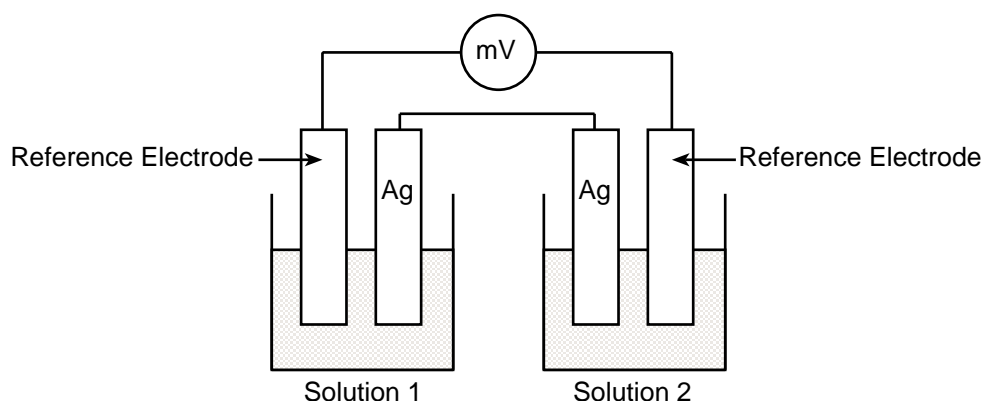
Two silver electrodes, connected by a copper wire, are immersed in two initially identical solutions, prepared by mixing 50 mL of 0.010 M $AgNO_3$ solution with 50 mL of 0.10 M NH_4NO_3 solution. Two identical reference electrodes are also immersed in the solutions and are connected through a millivoltmeter.

Note that the potential difference between the two solutions will be measured by the millivoltmeter.

0.10 M ammonia solution is added progressively to Solution 2. The complex ion $[Ag(NH_3)_2]^+$ is formed, and the potential difference is measured as a function of the volume of ammonia solution added. The results were as follows:

V (mL)	20	30	40	50
E (mV)	195	222	239	252

a)   Give a balanced redox half-equation for the processes occurring in both solutions 1 and 2, indicating which one represents oxidation and which represents reduction.

b)   Write a balanced redox equation for the overall process occurring in this system. Calculate $E°_{cell}$ for the system.

c)   With particular reference to the value you obtained for $E°_{cell}$ in part (b), explain the existence of potential difference between Solutions 1 and 2 observed.

d)   Calculate the overall stability constant K_{stab} for $[Ag(NH_3)_2]^+$.

e)   Derive an expression to give E (the potential observed in millivolts) in terms of V (the volume of ammonia added in mL).

f)   Use your answer to part (e) above to determine the number of mL of ammonia needed to increase the potential to 1.00 V.

Question 3 (20 minutes)

Molecular Orbital (MO) theory was introduced by Mulliken in the 1940s and 1950s, for which he won the 1964 Nobel Prize in Chemistry. It allows for the prediction of bond orders and paramagnetism of simple molecules.

a)   Draw and label the σ_{1s} bonding and antibonding molecular orbital surface diagrams. State qualitatively what makes one bonding and the other antibonding.

b)   Give the MO configurations and relative energy diagrams for H_2, H_2^-, He_2 and He_2^-. Which of these species are expected to have the same stability?

c)   Write down the electron configuration of the first excited state of H_2. Predict whether the molecule will stay bound or dissociate.

d)   It is difficult to obtain He_2 in its ground state, but it has been observed in its excited states. Explain how this is possible.

e)   Show that dioxygen, O_2, is a biradical species.

f)   In analytical chemistry the Hg^{2+} ion is identified by reduction to Hg^+. However, the actual structure of the latter as determined by X-ray analysis is found to be the dimeric Hg_2^{2+} species. Using MO theory, show why the dimeric species Hg_2^{2+} is more stable than the monomer Hg^+.

Question 4 (25 minutes)

a)   Name the following coordination compounds.

(i) $[PtCl_2(en)]$

(ii) $K_3[Fe(CN)_6]$

(iii) $[Co(NO_2)_2(NH_3)_4]_2SO_4$

(iv) $[Co(en)_3][Cr(C_2O_4)_3]$

b)   How many stereoisomers are possible for each of the following three species? Sketch them.

(i) $[Pd(SCN)_2(NH_3)_2]$

(ii) $[CoCl(H_2O)(en)_2]^{2+}$

(iii $[PtBrCl(NH_3)(CH_3NH_2)]$

(iv)   Which of the above three species would be expected to exhibit linkage isomerism? Sketch all of the possible linkage isomers for the *cis* form of the complex.

c)   Consider the bidentate ligand $H_2NCH_2CH_2N(CH_3)_2$ (dmen). What type of isomerism, if any, could be exhibited by a four-coordinate complex of the type $[M(dmen)_2]$? Sketch the isomers.

d)   For each of the metal ions in the following complexes (i) construct a clearly labelled d-orbital splitting diagram, (ii) calculate the associated 'spin only' magnetic moment and (iii) calculate the crystal field stabilisation energy (CFSE) in terms of Δ_O (assuming a regular geometry): $[MnCl_4]^{2-}$, $[Co(CN)_6]^{4-}$, $[Cu(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$.

e)   Is a regular geometry to be expected for all of the complexes listed in 1(d)? Explain. What affect, if any, does the deviation from a regular geometry have on the CFSE associated with the complex?

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**Question 5 (45 minutes)**   **Organic Section**

Students are to attempt ALL questions, (a) to (e). Spare pages are provided at the end of this section for further working, provided that any such working is clearly labelled with the question concerned and is neat and legible.

In all questions, you may assume an aqueous work-up with adjustment of pH as required.

(5 minutes)

a)   Which of the following compounds (if any) would you expect to rotate plane-polarised light?
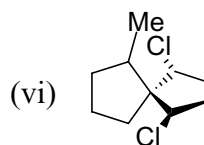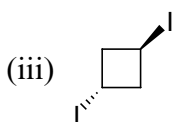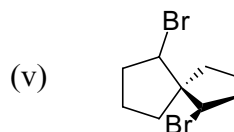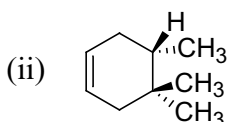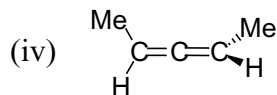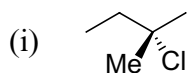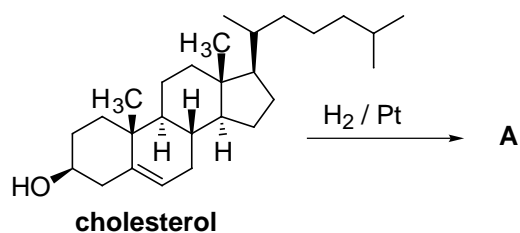

(8 minutes)

b)   Compound **X**, (*1R,6R*)-1-bromo-2,2,6-trimethylcyclohexane, reacts readily with sodium methoxide in methanol to give compound **Z** (C_9H_{16}). Isomer **Y**, (*1R,6S*)-1-bromo-2,2,6-trimethylcyclohexane, reacts only very slowly under these conditions.

   (i)   Draw compounds **X**, **Y** and **Z**.

   (ii) Explain their reactivities, using any appropriate diagrams or representations.

   (iii) Draw any other stereoisomers of **X** and briefly explain their expected reactivities.
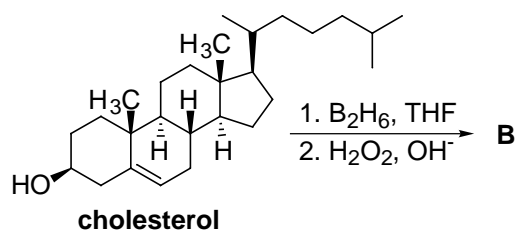
(7 minutes)

c)   Draw compounds **A** to **E**, the products you might expect from the following reactions of cholesterol. Pay particular attention to any stereo- or regiochemical issues, explaining any such selectivity.
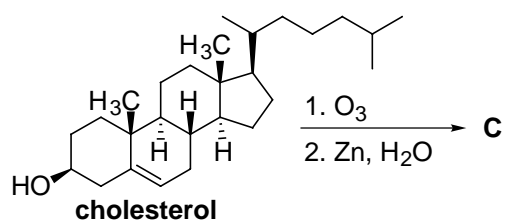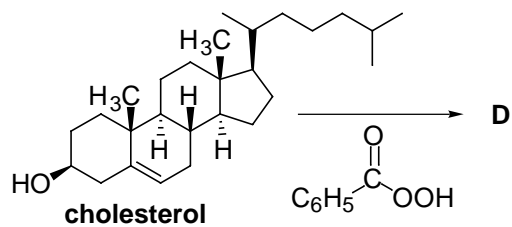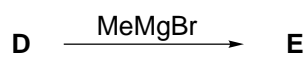
   (i)

(ii)

cholesterol

$\xrightarrow[\text{2. H}_2\text{O}_2,\ \text{OH}^-]{\text{1. B}_2\text{H}_6,\ \text{THF}}$ **B**

B

(iii)

cholesterol

$\xrightarrow[\text{2. Zn, H}_2\text{O}]{\text{1. O}_3}$ **C**

C

(iv)

cholesterol

$\xrightarrow{\hspace{3cm}}$ **D**

$\underset{\text{C}_6\text{H}_5}{\overset{\text{O}}{\text{C}}}$—OOH

D

(v)

D $\xrightarrow{\text{MeMgBr}}$ **E**

E

(15 minutes)

d)　A slightly unusual example of electrophilic aromatic substitution may be found in an interesting synthetic path to polycyclic aromatic compounds. Anthracene and many other such polycyclic molecules have been synthesised by a cyclisation reaction known as the Bradsher reaction or aromatic cyclodehydration. This method, developed by C.K. Bradsher, can be illustrated by the conversion of an *o*-benzylphenyl ketone to a substituted anthracene.


(F) R = Et
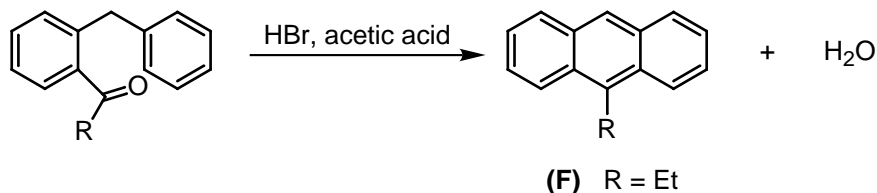
(i)　Using your understanding of electrophilic aromatic substitution, propose a mechanism for the Bradsher reaction.

(ii)　9-Ethylanthracene, compound (**F**), reacts with Cl_2 in the presence of a Lewis acid catalyst, such as $FeCl_3$. Give the structure(s) of the expected product(s) of this reaction, clearly explaining your reasoning.

(10 minutes)

e)　An interesting variant of the Aldol reaction is the Michael reaction, which involves the reaction of an α,β–unsaturated ketone or aldehyde with a ketone or aldehyde bearing α-hydrogens. It involves the nucleophilic attack of an enolate anion on the α,β–unsaturated carbonyl compound.

eg.
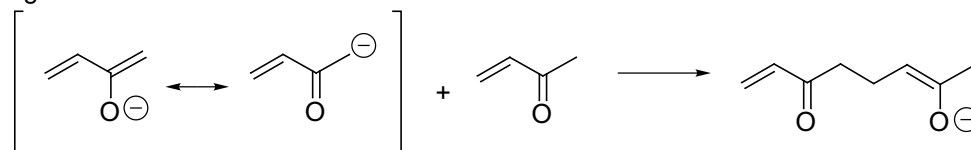
The Robinson annulation uses a Michael reaction and an Aldol condensation in a ring-forming process. Using this information, propose a mechanism for the following Robinson annulation.