

## PART A

2001

*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.*

### Instructions to Student

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 **black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

### Question 1 (20 minutes)

Molecular orbital theory is used to reconcile concepts such as resonance and magnetic properties of molecules which cannot be adequately explained by atomic orbital theory.

- a) Draw the molecular orbital energy diagram for  $\text{He}_2^+$ ,  $\text{He}_2$  (ground state) and  $\text{He}_2$  (1<sup>st</sup> excited state). State the bond order and the electron configuration of each species. Which ones would you expect to be stable?
- b) The homodinuclear species  $\text{B}_2$  and  $\text{O}_2$  are known to be paramagnetic. Use an MO orbital energy diagram to illustrate why. Are there any differences between the splitting of orbital energies in these two species? If so, why?

- c) Write out the electron configurations of  $B_2$  and  $O_2$ . Based on your answer in (b), predict which one would have a lower first ionisation energy compared to the corresponding atom's first ionisation energy.
- d) We have considered the effects of reducing a dimension on chemistry from Flatlandia. Let us now investigate the effects of adding a dimension. In the hypothetical 4<sup>th</sup>-landia, electrons are described using five, not four, quantum numbers.  $n$ ,  $l$ ,  $m_l$  and  $m_s$  remain as they are. The fifth number  $m_h$  (the "hyper" magnetic quantum number) behaves like  $m_l$ . The values of  $m_l$  DO NOT affect  $m_h$ . Eg if  $l = 3$ ,  $-3 \leq m_l, m_h \leq 3$ ; if  $l = 4$ ,  $m_l = 2$ ,  $-4 \leq m_h \leq 4$ .
- Predict the total number of elements expected in the first four periods.
- e) Consider  $SO_4^{2-}$ . Using both atomic and molecular orbital theory account for its structure. Include in your answer a hybrid orbital diagram and a molecular orbital energy diagram. Which orbitals does the sulfur atom use to form molecular orbitals? How many electrons are involved in bonding orbitals?

### Question 2 (25 minutes)

- a) For each of the following species draw the Lewis structure and predict the electron pair geometry and molecular shape:  $XeF_2$ ,  $ICl_3$  and the diprotic acid  $H_3PO_3$ . What is the hybridisation of the central atom in each of these species? Which of these species would be expected to have a dipole moment?
- b) Like 1,2-diaminoethane (en) the following related ligands containing phosphorus donor atoms are also potent chelating agents: (2-aminoethyl)dimethylphosphine (PN)  $[H_2NCH_2CH_2P(CH_3)_2]$  and 1,2-bis(diphenylphosphino)ethane (dppe). How many stereoisomers are possible for each of the following species containing these ligands? Sketch and name them.
- (i)  $[Pt(SCN)_2(dppe)]$
- (ii)  $[RuCl_2(dppe)_2]$
- (iii)  $[Co(PN)_3]^{3+}$
- (iv) Which, if any, of these species would be expected to exhibit linkage isomerism? Sketch all of the possible linkage isomers.
- c) Consider the bidentate ligand (2-aminoethyl)methylphenylphosphine (PN\*). What type of isomerism, if any, could be exhibited by a square planar complex of the type  $[M(PN^*)_2]$ ? Sketch the isomers.

### Question 3 (45 minutes)

*Data for this question can be found at the end of the question.*

Our adventure into the world of analytical chemistry begins on a different planet, Ammonica. The world of Ammonica is similar in many ways to our own, except for the fact that their various life forms are based around ammonia (which exists as a liquid under Ammonica's environmental conditions) instead of water.

- a) Just as the autodissociation of water (and its dissociation constant,  $K_w$ ) is so crucial to the people of Earth, so too is the autodissociation of ammonia to the Ammonites. The process of autodissociation now involves the transfer of a proton from one molecule of ammonia to another: ie,



with equilibrium constant  $K_{am} = 1.0 \times 10^{-22}$  at ambient conditions. (The notation (am) indicates that the species is present as an ammoniacal solution). The special symbols pH and pNH<sub>2</sub> are given to the values of  $-\log_{10}[NH_4^+]$  and  $-\log_{10}[NH_2^-]$  respectively. The definition of acidity and basicity constants in Ammonica is analogous to our own system, with the hydrogen ion and hydroxide ion concentrations replaced by ammonium and amide ion concentrations respectively.

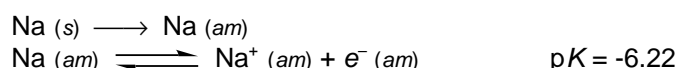
- (i) Calculate the pH of neutral ammonia.

Water (a solid the Ammonites find has an unbearable odour when dissolved) was dissolved in liquid ammonia to give a solution with  $[\text{H}_2\text{O}]_{\text{total}} = 0.10 \text{ M}$ .

- (ii) Adapt the Arrhenius definition of acids and bases on Earth to Ammonica.  
 (iii) Why would water be considered an acid in Ammonica?  
 (iv) Give the overall equation for the reaction between water and ammonia, and the expression for its equilibrium constant  $K_a(\text{H}_2\text{O})$ .  
 (v) Calculate the values of pH and  $\text{pNH}_2$  for the solution above under ambient conditions.  
 (vi) Calculate the change in pH effected by the addition of  $1.00 \times 10^{-3}$  moles of ammonium chloride to 1.0 L of this solution.

Solid sodium hydroxide (2.0 g) was added to 1.0 L of the solution to create a buffer based on the  $\text{H}_2\text{O} / \text{OH}^-$  acid / base pair.

- (vii) Calculate the pH of this solution and the change in pH that would occur upon addition of  $1.00 \times 10^{-3}$  moles of ammonium chloride. Comment on your answer with respect to your answer to part (vi) above.
- b) The partial pressure of ammonia gas,  $p(\text{NH}_3)$ , in the atmosphere of Ammonica is 0.020 atm. By coincidence, the atmospheric pressure in Ammonica is identical to that on Earth.
- (i) Calculate the equilibrium constant,  $K_{\text{vap}}$ , for the vaporisation of ammonia at the ambient temperature of Ammonica.  
 (ii) Calculate the ambient temperature on Ammonica.
- c) Liquid ammonia has a number of interesting and unusual properties, not least of which is its ability to support electrons in solution. Sodium (among other metals) will dissolve in liquid ammonia to give a solution containing both sodium ions and electrons in ammoniacal solution:



Organic chemists make use of this extraordinary fact here on Earth to reduce alkynes to alkenes; for example, 3-hexyne can be reduced to *trans*-3-hexene by adding it to a solution of sodium in liquid ammonia. A chemist on Ammonica dissolves 17.4 mg of sodium metal in 1.0 L of ammonia. To this solution, they carefully add 30 mg of 3-hexyne.

- (i) Give a balanced equation for the reduction of 3-hexyne in ammonia by ammoniacal electrons.  
 (ii) Calculate the initial concentration of electrons and ammoniacal sodium atoms in the solution.  
 (iii) Calculate the potential of the hexyne / hexene couple at the point where half of the 3-hexyne has been converted to *trans*-3-hexene.  
 (iv) Calculate the amount of 3-hexyne remaining in solution once the system has come to equilibrium and hence the maximum yield of the reduction product, *trans*-3-hexene under these conditions. Give your answer to as many significant figures as are necessary to illustrate a deviation from 100%.

**Data:**  $\text{p}K_a(\text{H}_2\text{O (am)}) = 4.75$   
 $\Delta G_{\text{vap}}^\circ(\text{NH}_3) = +5.84 \text{ kJ mol}^{-1}$   
 $\text{FW}(\text{Na}) = 22.99 \text{ g mol}^{-1}$

$$\begin{aligned} \text{FW}(\text{NaOH}) &= 40.00 \text{ g mol}^{-1} \\ \text{FW}(\text{C}_6\text{H}_{10}) &= 82.15 \text{ g mol}^{-1} \\ E^\circ (\text{C}_6\text{H}_{10}(\text{am}) / \text{C}_6\text{H}_{12}(\text{am})) &= +0.90 \text{ V} \end{aligned}$$

#### Question 4 (45 minutes)

- a)  $^{232}_{90}\text{Th}$  is one of the longest-lived radioactive isotopes, with a half-life of  $1.40 \times 10^{10}$  years.
- (i) The end product of the  $^{232}_{90}\text{Th}$  decay chain is  $^{208}_{82}\text{Pb}$ . A sample of ore is analysed and is found to contain 56.5mg of 208-lead for every gram of 232-thorium. Assuming that all other chain half-lives are much shorter and can therefore be ignored, how old is the rock?
- (ii) The longest-lived intermediate decay product of the thorium chain is the first member of the series,  $^{228}_{88}\text{Ra}$ , with a half-life of 5.76 years. How many grams of Ra-228 will be found in a sample of ore containing 1.000g of thorium?
- b) **Data:**  $C_v(\text{O}_2(\text{g})) = 24.0 \text{ J K}^{-1} \text{ mol}^{-1}$      $\Delta_f H^\circ(\text{H}_2\text{O}(\text{g})) = -242.00 \text{ kJ mol}^{-1}$ .

Gaseous Species	Average $C_p$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
$\text{H}_2$	30
$\text{N}_2$	33
$\text{H}_2\text{O}$	41

A perfect gas has internal energy  $U = 3/2(nRT)$ , and  $PV = nRT$ .

- (i) Show that molar constant-volume heat capacity,  $C_v = \frac{dq_v}{dT}$ , is equal to  $\frac{3}{2}R$  for a perfect gas.
- (ii) Determine a numerical ratio of molar constant pressure heat capacity  $C_p$  to  $C_v$  for a perfect gas. Qualitatively explain the reason for the difference in the two quantities. The ratio found holds approximately for many real gases. Using the ratio find  $C_p$  for gaseous  $\text{O}_2$ .

Hydrogen is burnt in air (20%:80%  $\text{O}_2$ : $\text{N}_2$ ) in a torch. It is assumed the system is adiabatic. Assume that the reaction takes place completely, and that 200% more air than the stoichiometric ratio is present.

- (iii) What is the composition of the exit mixture of gases?
- (iv) Using any data given or previously found, determine the maximum temperature reached by the flame (inlet temperature is 298.15K)?

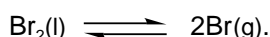
c) **Given:**  $\ln \frac{p_2}{p_1} = -\frac{\Delta_{\text{vap}} H^\circ}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$

**Data:**  $1 \text{ atm} = 101.3 \text{ kPa}$      $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$   
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$   
 $\Delta_{\text{diss}} S^\circ(\text{Br}_2(\text{g})) = 104.5 \text{ J K}^{-1} \text{ mol}^{-1}$ .

[Assume all enthalpies and entropies constant over the given temperature ranges, and that gases may be treated as ideal.]

Bromine is extremely toxic, and it presents a special hazard due to a very high volatility. At normal atmospheric pressure the boiling point of bromine is 59.2°C, and even at 9.3°C the pressure of vapours in a closed system is 13.33kPa.

- (i) Use these data to estimate the standard molar enthalpy of vaporisation of elementary bromine.
- The dissociation equilibrium of bromine is significant because of the low enthalpy of dissociation ( $\Delta_{\text{diss}} H^\circ = 192.9 \text{ kJ mol}^{-1}$ ), and because very low concentrations of bromine radical are enough to initiate chain reaction mechanisms.
- (ii) Evaluate the number of bromine atoms contained in saturated bromine vapour at boiling point and normal atmospheric pressure in a 1.000L vessel, and the percentage of atomic bromine in bromine vapours in these conditions.
- (iii) Consider the reaction



What is the equilibrium constant at 50°C? What is the vapour pressure of Br atoms above the liquid?

## ORGANIC SECTION (45 minutes)

### Question 5 (35 minutes)

The structure of an optically active hydrocarbon **A** was deduced from the following:

Treatment of **A** with hot concentrated acidified  $\text{KMnO}_4$  gave a single product, **B**, which upon heating with iodine in alkaline solution gave **C** ( $\text{C}_9\text{H}_{16}\text{O}_4$ ) and a yellow precipitate of iodoform. **C** can also be obtained from the following reaction scheme: 4-isopropyl-1,2-dihydroxybenzene was catalytically hydrogenated with a palladium on carbon catalyst under a pressure of 138 atm (2000 psi), forming **D**, and **D** treated with periodic acid in aqueous THF to form **C**.

- a) Give two possible structures for **A** consistent with this information, and draw out the reaction schemes, clearly labeling products **A-D** (do not show stereochemistry).

Addition of  $\text{HBr}$  to **A** in  $\text{CCl}_4$  results in an achiral product **E**.

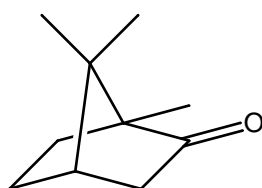
- b) Draw the single possible structure for **A** (do not show stereochemistry). Give the structure of **E** and explain why it is not chiral.

The main component of the essential oil of oranges, known as limonene (**F**) ( $\text{C}_{10}\text{H}_{16}$ ), is structurally very similar to **A**, and in fact hydrogenation of both limonene and **A** over a palladium on carbon catalyst gives the same product, p-menthane (**G**). Treatment of limonene with ozone followed by dimethyl sulfide produces formaldehyde (methanal) and **H**. Treatment of **H** with  $\text{I}_2/\text{NaOH}$  gives **J** and twice the amount of iodoform as **B** gave under the same conditions.

- c) Draw out this reaction scheme and clearly label products **A, B, F-H** and **J** (do not show stereochemistry).

Limonene (**F**) is a member of a family of compounds known as terpenes. In fact a number of different terpenoids (derivatives of terpenes) can be synthesized from limonene.

Hydration of limonene with an acid catalyst may result in the formation of two constitutionally isomeric bicyclic alcohols. One of them (**K**) upon treatment with sodium dichromate is oxidised to camphor (structure below), but the other (**L**) cannot be oxidized with sodium dichromate.



Camphor

- d) Draw the structures of **K** and **L** (do not show stereochemistry), and show a mechanism for their formation from limonene under an acid catalyst.

Dehydration of **L** with concentrated sulfuric acid can result in either of the two isomeric terpenes that are the main constituents of wood turpentine:  $\alpha$ - and  $\beta$ -pinene. When treated with hot concentrated  $\text{KMnO}_4$ , only  $\beta$ -pinene gives off carbon dioxide, and  $\alpha$ -pinene forms a keto acid. Interestingly although dehydration of **L** can give  $\alpha$ -pinene, if  $\alpha$ -pinene is treated with dilute sulfuric acid, **K**, and not **L** is formed.

- e) Draw the structures of  $\alpha$ - and  $\beta$ -pinene, and propose a mechanism for the formation of **K** from  $\alpha$ -pinene in the presence of dilute sulfuric acid.
- f) Is camphor chiral? Draw a diagram clearly showing either the reason you think camphor is not chiral, or all possible stereoisomers of camphor, assigning any stereocentres R or S.
- g) What would be the organic product or products formed when **A** is treated with the following reagents? If more than one product is possible, indicate which, if any, will be the major

product, and be sure to note any regiochemical and stereochemical consequences of these reactions.

- (i) bromine in  $\text{CCl}_4$ .
- (ii) iodine monochloride.
- (iii)  $\text{CHCl}_3$  in concentrated  $\text{KOH}$ .
- (iv) *m*-chloroperbenzoic acid followed by sodium hydroxide and acidic workup.
- (v) *m*-chloroperbenzoic acid followed by phenyl magnesium bromide and acidic workup.

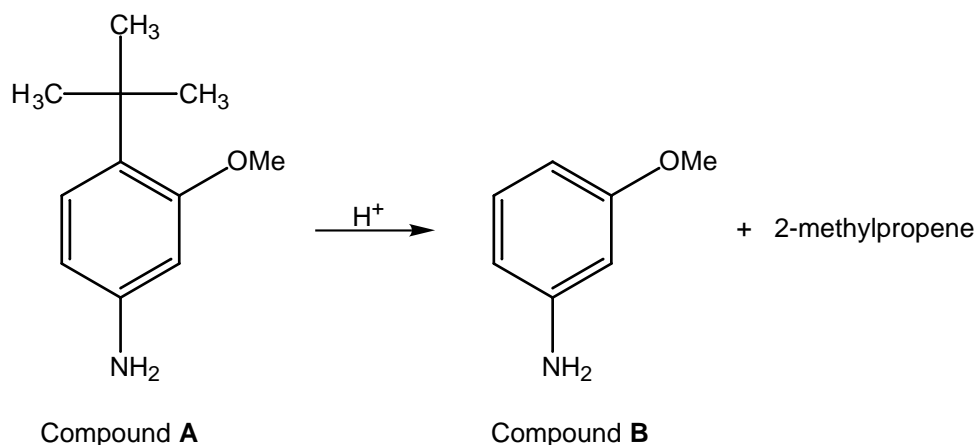
**Question 6 (5 minutes)**

Give the organic product or products of the following reactions, noting any stereochemical or regiochemical consequences:

- a) 1-butyne  $\xrightarrow[2. \text{H}_2\text{O}_2/\text{OH}^-]{1. \text{BH}_3 \cdot \text{THF}}$  ?
- b) 1-butyne  $\xrightarrow{\text{NaNH}_2}$  ?  $\begin{cases} \xrightarrow{\text{Et-Br}} ? \\ \xrightarrow{t\text{-Bu-Br}} ? \end{cases}$
- c) 1-butyne  $\xrightarrow{\text{H}_2/\text{Lindlar catalyst}}$  ?

**Question 7 (5 minutes)**

An inexperienced young chemist wanted to make compound **B**, shown below, and found a bottle of the structurally similar compound **A**, also shown below. Trying to convert **A** into **B** in one step and not really sure of how to do so, our adventurous young chemist decided to apply some classical trial and error, simply heated **A** with a catalytic amount of dilute acid, and was delighted when **B** was formed, as well as 2-methylpropene.



Propose a mechanism for this reaction.