

## AUSTRALIAN CHEMISTRY OLYMPIAD

### FINAL PAPER

### PART A

1990

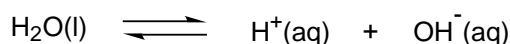
#### Instruction to candidates

- (1) You are allowed **10 minutes** to read this paper, and **2<sup>1</sup>/<sub>2</sub> hours** to complete the questions.
- (2) You are **not** permitted to refer to books, notes or periodic tables but you may use a non-programable electronic calculator and molecular models.
- (3) You must attempt **all** questions.
- (4) 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.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (6) Your name must be written in the appropriate place on **each page** of your answers.
- (7) Use **only black** or **blue ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

#### Question 1

Chemists find Gibbs energy a very useful quantity, for it links many experimentally useful quantities (equilibrium constants, cell emf, etc ) to fundamental thermodynamic quantities.

- (a) Derive an expression that shows for a system at thermodynamic equilibrium, that the equilibrium will shift to the right for an endothermic process when the temperature is increased.
- (b) Using the above expression determine  $\Delta H^\circ$  and  $\Delta S^\circ$  for the autoionization of water.



T (°C)	K ( $\times 10^{14}$ )
0	0.114
25	1.00

35	2.09
40	2.92
50	5.47

**Data:**  $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$   
 $= 8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$

### Question 2

The reaction,  $\text{N}_2\text{O}_5(\text{g}) \longrightarrow 2\text{NO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ , is first order in  $\text{N}_2\text{O}_5(\text{g})$ . The course of reaction was followed by monitoring the total pressure with the results shown below.

t (min)	$P_T$ (mm Hg)
0	350
10	490
20	592
40	718
60	788

Use the integrated rate law to calculate the rate constant, k.

### Question 3

- (a) (i) For each of the following interhalogen species draw the Lewis structure and predict the electron pair geometry and molecular shape:  $\text{BrF}_3$ ,  $\text{ICl}_4^-$  and  $\text{IF}_5$ .

What is the hybridisation of the central atom in each species?

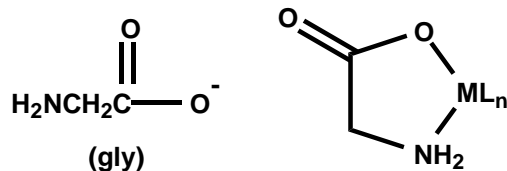
Which of the species would be expected to have a dipole moment?

- (ii) The ions  $\text{O}_2^-$ ,  $\text{O}_2^{2-}$  and  $\text{O}_2^+$  occur in several compounds, for example, in potassium superoxide ( $\text{KO}_2$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and dioxygenyl hexafluoroplatinate(V) ( $\text{O}_2^+ [\text{PtF}_6]^-$ ), respectively.

Compare these three ions with  $\text{O}_2$  by listing the four in order of increasing bond length.

Which of these four species would be expected to be paramagnetic?

- (b) (i) Using crystal field theory explain why the hexaaquanickel(II) and tetrachloronickelate(II) ions exhibit paramagnetic behaviour whereas the tetracyanonickelate(II) ion is diamagnetic.
- (ii) Many trace metal ions exist in the bloodstream as complexes with amino acids or small peptides. For example, the anion of the amino acid glycine, the glycinate ion (gly), is known to coordinate to a variety of transition metal ions as a bidentate ligand, as shown below:



Sketch all the possible stereoisomers for the following glycinate complexes:

- (i)  $[\text{Zn}(\text{gly})_2]$  (tetrahedral)

- (ii)  $[\text{Pt}(\text{gly})_2]$  (square planar)

- (iii)  $[\text{Cr}(\text{gly})_3]$  (octahedral)

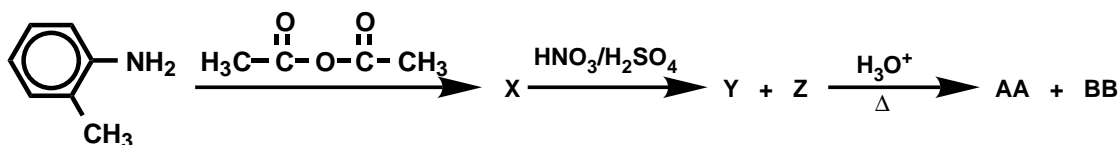
Use to represent the ligand.

#### Question 4

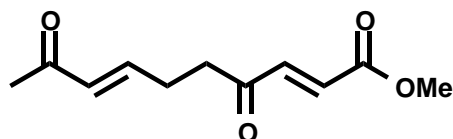
- (a) (i) Ethers can be prepared by the Markovnikov addition of alcohols to alkenes in the presence of strong acids which have non-nucleophilic conjugate bases. tert-Butyl ethers,  $\text{H}_3\text{C}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{OR}$ , are often prepared in this way.

Write a complete mechanism for the addition of methanol to 2-methylpropene in the presence of fluoroboric acid ( $\text{HBF}_4$ ).

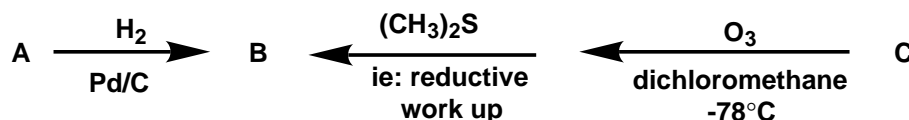
- (ii) Why must the acid, used as a catalyst, in this case  $\text{HBF}_4$ , have a non-nucleophilic conjugate base?
- (b) (i) Complete the following sequence of reactions by identifying compounds **X**, **Y**, **Z**, **AA** and **BB**.



- (ii) Write a mechanism for the formation of compounds **Y** and **Z** from compound **X**.
- (c) Compound **A**, is a degradation product of the antibiotic vemiculine, and has the following structure.

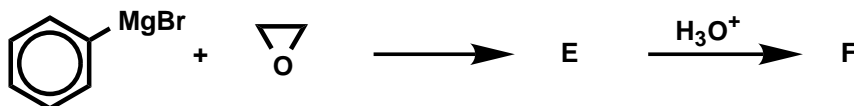


The structure was confirmed by converting **A** into compound **B**,  $\text{C}_{11}\text{H}_{18}\text{O}_4$ , which could also be prepared by ozonolysis of compound **C**,  $\text{C}_{11}\text{H}_{18}\text{O}_2$ .



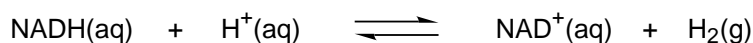
Assign structures to **B** and **C**, and give systematic (IUPAC) names to both compounds.

- (d) Grignard reagents are best known for their reaction with carbonyl groups. However they will react with other electrophiles including oxirane (ethylene oxide). Predict the products **E** and **F** of the following reaction.



#### Question 5

Nicotinamide adenine dinucleotide (NAD) is an important electron transport agent in biochemistry. It exists in an oxidised form ( $\text{NAD}^+$ ) and a reduced form (NADH). The two forms are formally related by the equation:



The standard reduction potential for the reduction of  $\text{NAD}^+$  is:



- (a) In a biological system with a pH of 8.2, the cell potential is -0.20 V when the ratio of oxidised to reduced forms of NAD is 0.2. What is the hypothetical "H<sub>2</sub> pressure" in the system?
- (b) In biological systems, the standard state of H<sup>+</sup>: [H<sup>+</sup>] = 1M is unrealistically acidic. It is more convenient to define a biochemical standard state in which pH = 7 and similarly for further convenience, all other species have standard state concentrations of 1mM rather than 1M.

Calculate  $E_{\text{cell}}^{\circ}$  for these new biochemical standard states at 25°C.

- (c) What can be said about  $E_{\text{NAD}^+; \text{NADH}}^{\circ}$  at the biochemical standard state?

### Question 6

Paper electrophoresis at pH 6.0 was carried out on a mixture of glycine, alanine, glutamic acid, lysine, arginine and serine.

- (a) Which compound(s) moved fastest towards the anode?
- (b) Which moved fastest towards the cathode?
- (c) Which remained at or near the origin?