AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART B

1992

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 or notes but you may use a non-programable electronic calculator and molecular models.

(3) You must attempt **all** questions.

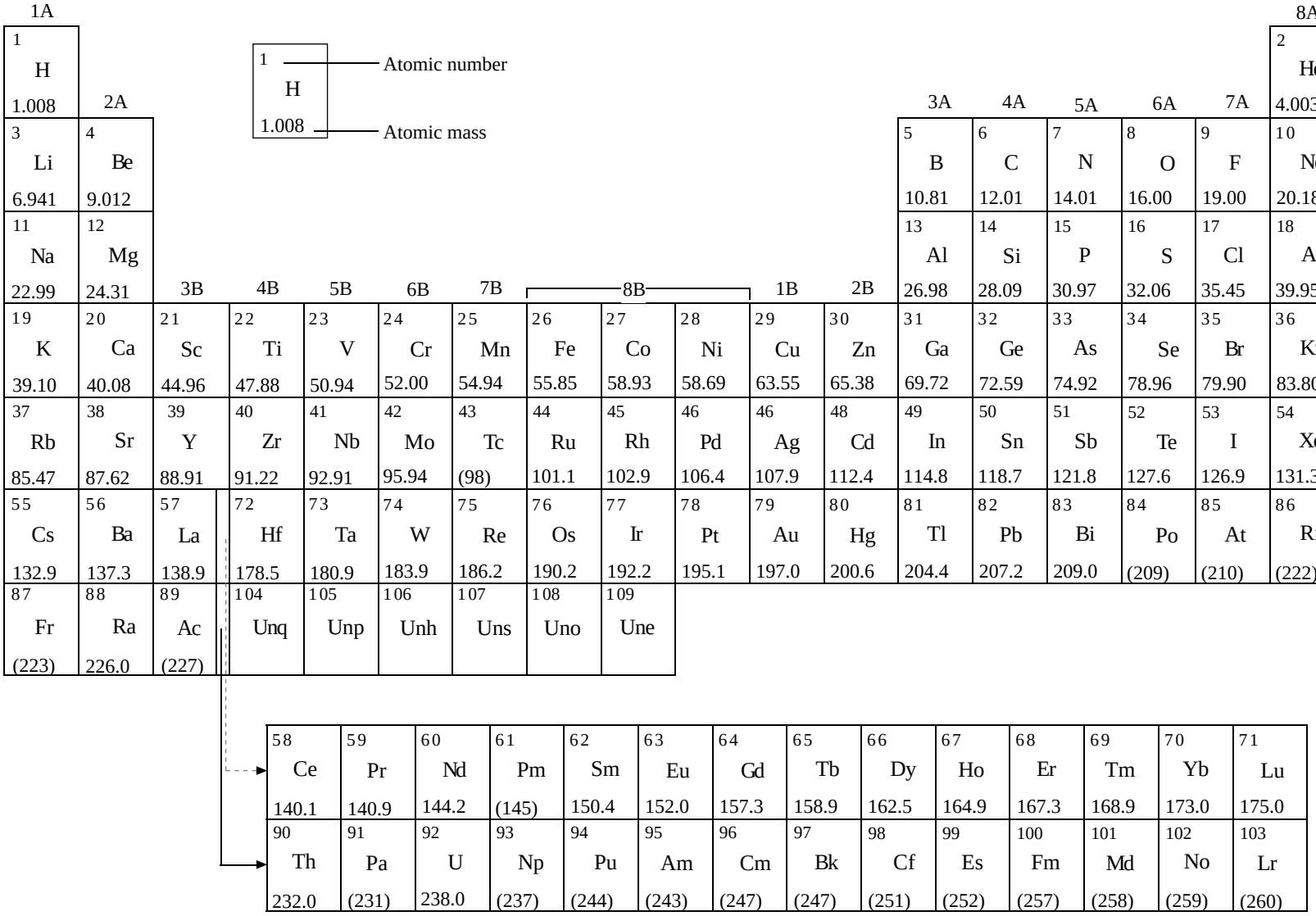
(4) Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the backs of pages. Only material presented in the answer boxes will be assessed.

(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.

Periodic Table of the Elements



Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

Question 1

(a) The following gas phase reactions are known to occur at varying temperatures.

$n\text{-}C_4H_{10} \longrightarrow (CH_3)_2C = CH_2 + H_2$

$C_2H_4 + Cl_2 \longrightarrow CH_2ClCH_2Cl$

$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$

Given the following bond energies

Bond	Bond energy (kJ)
C—H	413
C—C	347
C=C	614
H—H	432
C—Cl	339
C—O	358
O—H	467
Cl—C	239
O—O	146
O=O	495

(i) Predict the approximate values of the heats of reaction and specify which are exothermic and which are endothermic.
(ii) For each reaction specify whether the entropy change is negative or positive.
(iii) Indicate if a reaction would be reversible, and what role pressure would play in the equilibrium.

(b) In an investigation of the kinetics of the catalytic decomposition of NH_3 into its elements at 1100°C, the following half lives of NH_3 samples (with no N_2 or H_2 initially present) and respective initial partial pressures of NH_3 were found.

Half life (minutes)	7.6	3.7	1.7
Initial partial pressure of NH_3 (atmospheres)	0.349	0.171	0.076

(i) Determine the order of the reaction
(ii) Determine the rate constant of decomposition.

Question 2

Charged species such as hydrated metal ions do not generally have an appreciable solubility in non-polar liquids. However, if the metal ion forms a neutral complex with an organic ligand, the hydrophobic metal-ion complex is often much more soluble in organic solvents. When an aqueous solution of metal ion is shaken with an immiscible organic solvent containing such an organic ligand, the metal-ion complex is distributed between the two phases.

This equilibrium process is characterised by the **Distribution Ratio**, **D** where

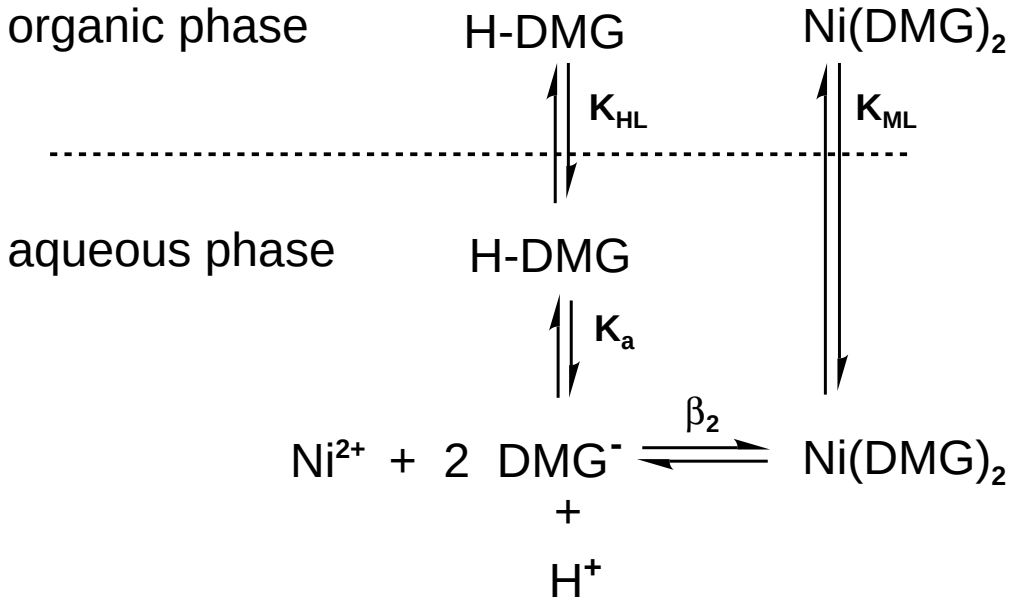
$$\mathbf{D} = \frac{\text{[total concentration of all forms of metal ion in the organic phase]}}{\text{[total concentration of all forms of metal ion in the aqueous phase]}}$$

The experimental procedure is known as **solvent extraction**. One widespread application of solvent extraction is to use a ligand which forms a *coloured* complex with the metal ion. In this way, a metal ion in a very dilute solution (say $Ni^{2+}_{(aq)}$ in tap water) can be concentrated by solvent extraction (or separated from other metal ions) as a coloured complex into a much

smaller volume of an organic solvent. This more concentrated, coloured organic solution might then be analysed using visible spectrophotometry for example.

Often, the organic complexing agent is a weak acid (HL), whose conjugate base is the ligand (L^-). Protons and metal ions compete for L^-, so the fraction of metal ion which is extracted into the organic solvent is pH-dependent.

The equilibria involved in this process are shown schematically below, for a specific example. Nickel(II) forms a very thermodynamically stable complex (log β_2 = 17.72) in water with the conjugate base of dimethylglyoxime. Dimethylglyoxime is a very weak monoprotic acid (pK_a = 10.66) in water. The intensely red bis(dimethylglyoximato)nickel(II) is quite soluble in organic solvents so very low levels of Ni(II) can be can be spectrophotometrically determined after complexation with DMG and extraction into chloroform.



In this example, the red nickel complex is much more soluble in the chloroform phase than in water:

$$K_{ML} = \frac{[Ni(DMG)_2]_{org}}{[Ni(DMG)_2]_{aq}} = 300$$

while dimethylglyoxime is only slightly more soluble in the organic phase than in water:

$$K_{HL} = \frac{[H\text{-}DMG]_{org}}{[H\text{-}DMG]_{aq}} = 3$$

Note that the charged species, H^+, Ni^{2+} and $DMG^-_{(aq)}$ are not at all soluble in chloroform (as expected).

(a) After writing down expressions for all the equilibrium constants in this system, express $[Ni(DMG)_2]_{org}$ in terms **only** of $[Ni^{2+}]$ and $[DMG^-]$ and relevant equilibrium constants.

(b) Express $[DMG^-]$ in terms **only** of $[H^+]$ and $[H\text{-}DMG]_{org}$ and relevant equilibrium constants.

(c) Express **D** in terms **only** of $[H^+]$ and $[H\text{-}DMG]_{org}$ and relevant equilibrium constants. You may assume that $[Ni^{2+}] >> [Ni(DMG)_2]_{aq}$.

(d) Express the fraction of Ni(II) which remains in the water phase in terms **only** of **D** and the volumes of the two phases.

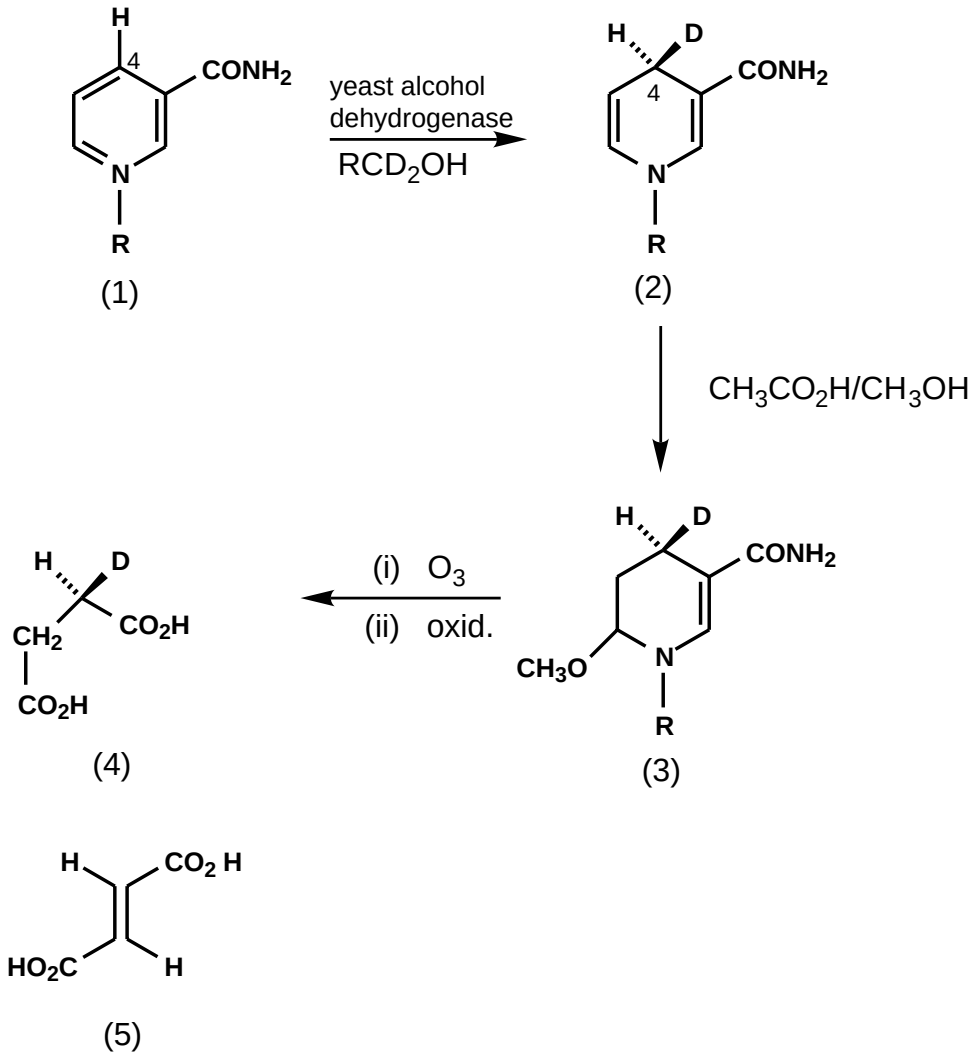
(e) Calculate the concentration of nickel which remains in the aqueous phase when 1L of 10^{-4} M Ni^{2+} at pH 5.0 is extracted with 50 mL chloroform containing 0.01M dimethylglyoxime.

Question 3

Alcohol dehydrogenases are enzymes which catalyse the transfer of a hydrogen from a substrate alcohol to a coenzyme (NAD^+) (1). In the process the NAD^+ is reduced to NADH (2) the hydrogen being added stereospecifically to one face of (1). The face chosen depends upon the exact nature of the enzyme. Using suitably deuterated alcohols as substrates it is possible to probe the stereochemistry of the hydrogen transfer. The resulting coenzyme (2) can chemically degrade as shown to afford a stereospecifically deuterated succinic acid (3). This is illustrated in Scheme 1 for yeast alcohol dehydrogenase.

A newly isolated alcohol dehydrogenase has been probed by this method, and a specifically deuterated succinic acid of unknown stereochemistry isolated from the chemical degradation. Further analysis shows that this is chemically and optically identical with a reference sample of monodeuteration succinic acid obtained by the enzymatic <u>anti</u> addition of D_2O to (E)-but-2-ene-1,4-dioic acid (5) followed by chemical removal of the alcohol group from the intermediate (2S,3X-deuterio 2-hydroxybutan-1,4-dioic acid).

Scheme (1)



(E)-but-2-endioic acid

Note: When D_2O is added to olefins under biological conditions the deuterium bond to oxygen is labile and easily lost only C-bonded deuterium remains.

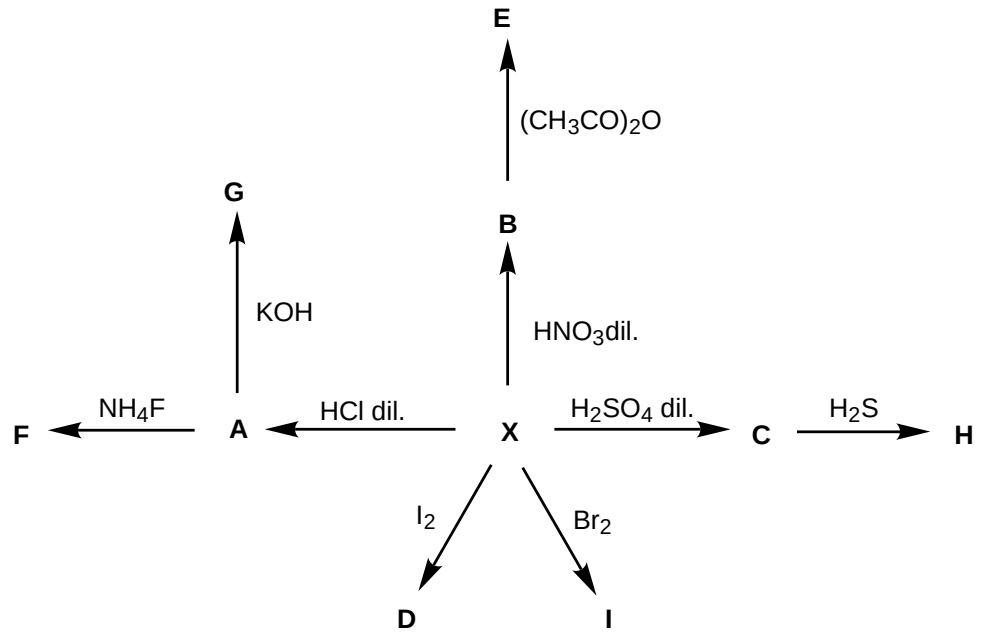
a) Using Fischer formulae, write down the structure of 2S,3X-deuteriomalic acid obtained and indicate if X corresponds to a R or S configuration.

b) Indicate the 4R or 4S stereochemistry of the reduced deuterated coenzyme.

c) Indicate if the hydrogen transfer occurs from the Si or Re face of the coenzyme.

Question 4

X is a metal. Some of the reactions to prepare its compounds are given in the following scheme:



The selenide of **X**, prepared by heating **X** in a current of H_2Se and subliming the product in hydrogen at a dull red heat, contains 41.26% of Se.

a) Determine the relative atomic mass (atomic weight) of **X**, and identify the element.

b) Give the formulae of compounds **A** to **I** and write balanced equations for their formation.

c) To a 0.020 mol/dm^3 solution of $\mathbf{X}^{2+}$ ions, 0.200 moles of NH_3 were added with formation of $[\mathbf{X}(NH_3)_4]^{2+}$ ions. Calculate the amount of KI to be added in order to keep the concentration of $[\mathbf{X}(NH_3)_4]^{2+}$ equal to 3.5 x 10^{-6} mol/dm^3 and the molar concentrations of all species at the equilibrium. (K_{stab} for $[\mathbf{X}(NH_3)_4]^{2+}$ and $[\mathbf{X}I_4]^{2-}$ are 4.0 x 10^6 and 1.25 x 10^6, respectively).

Question 5

Ambucaine ($C_{17}H_{28}N_2O_3$) is a local anaesthetic derived from benzoic acid. Its infra-red spectrum shows an absorption near 1730 cm^{-1} and ambucaine dissolves in dilute mineral acid.

The synthesis starts with the nitration of methyl benzoate using a sulfuric-nitric acid mixture. Subsequent saponification ($NaOH/H_2O$) of the nitrated product followed by neutralisation of the resulting sodium salt, yields **A** ($C_7H_5NO_4$). Catalytic reduction of **A** with hydrogen in the presence of palladium affords **B** which unlike **A** is soluble in dilute mineral acid. Reaction of **B** with nitrous acid followed by heating in water gives **C** ($C_7H_6O_3$) which gives a violet colouration with ferric chloride solution. Further nitration of **C** gives **D** which reacts with ethanol in the presence of a trace of concentrated acid to give **E** ($C_9H_9NO_5$), which is soluble in cold aqueous sodium hydroxide but not sodium bicarbonate. **E** reacts with potassium hydroxide and 1-bromobutane to yield **F** ($C_{13}H_{17}NO_5$) which is no longer soluble in cold dilute sodium hydroxide. Saponification of **F** with aqueous KOH, yields **G** which is reacted firstly with thionyl chloride ($SOCl_2$) to give **H**. It in turn is reacted with 2-(N,N-diethylamino)ethanol to afford **I** ($C_{17}H_{26}N_2O_5$) which upon catalytic hydrogenation (H_2/Pd) affords Ambucaine.

(a) Deduce the structures of compounds A to **I** and hence the structure of Ambucaine.

(b) Proposed a reasonable mechanisms to account for the conversion of **E** to **F** and **G** to **I**.