FINAL PAPER

PART B

1993

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 5 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 nonprogrammable electronic calculator and molecular models.

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

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

(5) 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.

(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

(a) The kinetics of the gas phase reaction between carbon monoxide and nitrogen dioxide yielding carbon dioxide and nitrogen monoxide (reaction A) has been studied.

(i) Write the equation for this reaction.

(ii) Show that if the volume of the reaction vessel (for reaction A) is kept constant, the total pressure will depend only on the temperature.

(iii) Express the reaction rate in terms of the time dependence of the concentration for all molecules participating in reaction A.

(b) In an investigation of reaction A at 430°C two series of measurements were carried out.

	Concentration carbon monoxide (M)	**Concentration nitrogen dioxide (M)**	**Rate of reaction ($M\ s^{-1}$)**
Series 1:	0.10	0.10	0.012
	0.20	0.10	0.024
	0.30	0.10	0.036
	0.40	0.10	0.048
Series 2:	0.10	0.20	0.024
	0.20	0.20	0.048
	0.30	0.20	0.072
	0.40	0.20	0.096

(i) Show that the reaction is of order one with respect to each of the reactants.

(ii) Write the complete rate expression, and state the total order of the reaction.

(iii) Calculate the rate constant at 430°C and give its units.

(c) As a foundation for understanding the mechanism of reaction A, we want to envisage the electronic structure and molecular geometry of all molecules participating in the reaction.

(i) Write the electron dot (Lewis) structure for carbon monoxide, carbon dioxide, nitrogen monoxide, and nitrogen dioxide (ONO; the unpaired electron on nitrogen).

(ii) Two of the molecules in (i) can exhibit paramagnetism. Which ones? Explain your reasoning.

(iii) Use the valence-shell-electron-pair-repulsion model to indicate a probable geometry of the molecules in (i).

(iv) One of the molecules in (i) does not have an electric dipole moment. Which one? Explain your reasoning.

(d) If we have a large excess of one of the reactants, the reaction A will appear to be of order one.

Calculate the half-life of carbon monoxide at 650 K when nitrogen dioxide is in large excess relative to carbon monoxide. The rate constant under the existing conditions is 4.40 s^{-1}.

(e) In a table of thermodynamic data we find (data in kJ mol^{-1} at 25 °C):

	$H_f°$	$G_f°$
Carbon dioxide	-393.5	-394.4
Carbon monoxide	-110.5	-137.3
Nitrogen dioxide	33.8	51.8
Nitrogen monoxide	90.4	86.7

(i) Calculate $\Delta H°$, $\Delta G°$, and $\Delta S°$ for reaction A at 25 °C.

(ii) Is the reaction between carbon monoxide and nitrogen dioxide spontaneous at 25 °C? Explain your reasoning.

Question 2

a) Predict the shapes of the following molecules, and then predict which you would expect to have resultant dipole moments and which are nonpolar.

(i) C_2H_4

(ii) CS_2

(iii) NH_3

(iv) H_2S

(v) SF_6

(vi) SO_2

(vii) $BeCl_2$

(viii) $SnCl_2$

b) The five coordinated complex Ab_3c_2 has a trigonal bipyramidal structure. (A is the central atom, b and c are ligands.) Draw all stereoisomers of the complex.

Question 3

(a) Sodium carbonate is produced in the so-called Solvay process. The overall reaction for this process is

$$CaCO_3 + 2NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

However, this direct reaction between calcium carbonate and sodium chloride does not take place.

Can we draw any conclusions about thermodynamic and/or reaction kinetic conditions for this assumed reaction?

The Solvay process accomplishes this overall reaction indirectly.

(b) A first step in the Solvay process is the thermal decomposition of calcium carbonate into calcium oxide and carbon dioxide. The decomposition pressure (under equilibrium condition) of carbon dioxide is 0.50 atm at 855°C and 1.00 atm at 900°C.

(i) Write the equation for the decomposition reaction and indicate the states of the participating compounds.

(ii) What is the equilibrium constant (including units) for the decomposition reaction at 855°C and 900°C, and what conditions must be fulfilled in order for equilibrium to be established?

(iii) Calculate $\Delta G°$ for the reaction at 855°C and 900°C.

(iv) Assume $\Delta H°$ and $\Delta S°$ to be temperature independent quantities. Calculate $\Delta H°$ and $\Delta S°$ for the reaction.

Indicate whether the reaction is exothermic or endothermic.

(v) Explain briefly why $\Delta S°$ for the decomposition is positive.

(vi) Show that $K \approx 10^{-22}$ atm for the reaction at 25°C. Is the decomposition of calcium carbonate a spontaneous reaction at 25°C when the partial pressure of carbon dioxide in the atmosphere is set equal to 0.03 atm at ground level?

Explain your reasoning.

Question 4

(a) In 1923, P. Debye and E. Hückel derived the following equation that permits the calculation of the activity coefficients, f_X, of ions from their charge, Z_X and effective diameter (a_X, in Ångstrom units) of the hydrated ion and the ionic strength of the solution, I.

$$-\log f_X = \frac{0.51\, Z_X^2 \sqrt{I}}{1+0.33\, a_X \sqrt{I}}$$

Hydrated cations have effective diameters of approximately 8Å and hydrated anions are smaller, usually 5Å in diameter.

(i) Use this information and the Debye-Hückel relationship to calculate the solubility of zinc(II) hexacyanoferrate(III) in a 0.0333M solution of magnesium perchlorate.
The thermodynamic K_{sp} for the zinc salt is 4.1×10^{-16}.

(ii) What error is introduced into your answer if the cation diameter is 6Å instead of 8Å?

(b) Consider the high temperature equilibrium dissociation of bismuth dimers:

$$Bi_2 \rightleftharpoons 2\,Bi$$

(i) Derive an expression which relates the equilibrium constant K_p to only the total pressure, P and the degree of dissociation, α, and use it to calculate the values of K_p in the following table:

T (K)	**P (Pa)**	α	**Kp**
1148	41.9	0.347	
1195	105.9	0.418	

(ii) Use an equation relating the temperature dependance of Kp to calculate the dimerisation enthalpy of bismuth. Explain the assumptions, if any, you needed to make.

Question 5

A compound **A** (C_5H_8O) is an unsaturated, optical active aldehyde with S-configuration.

When the compound is treated with 1) phenyl magnesium bromide and 2) H_3O^+, compound **B** ($C_{11}H_{14}O$) is obtained. **B** is then treated with 3) BH_3 and 4) H_2O_2 in alkaline solution, and the compound **C** is formed. **C** is oxidised with chromic acid giving **D** ($C_{11}H_{12}O_3$). Reduction of **D** with Zn(Hg) in hydrochloric acid gives the compound **E**.

When **E** is heated with small amounts of phosphoric acid an electrophilic cyclisation occurs to afford the ketone **F** ($C_{11}H_{12}O$).

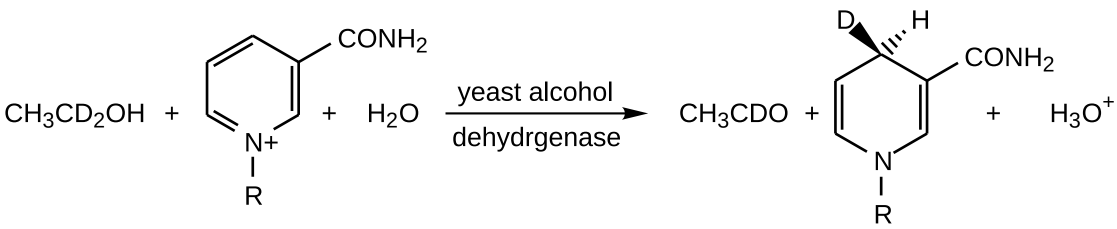
a) Give the structural formulas for the compounds **A** $\rightarrow$ **F**.

b) Give also rational names including R,S-configurations for all the compounds.

c) Give reaction mechanisms for the steps involved in the conversion of **A** to **E**.

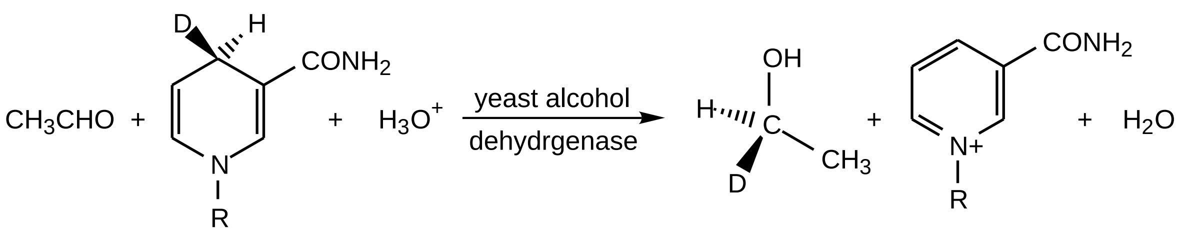
Question 6

The coenzymes nicotinamide adenine dinucleotide, NAD^+, and nicotinamide adenine dinucleotide phosphate, $NADP^+$, are associated with a large number of enzymes known as dehydrogenases. A typical reaction catalysed by dehydrogenase found in the liver (liver dehydrogenase) is the oxidation of ethanol to acetaldehyde. Yeast alcohol dehydrogenase acts in the same way. For example, if ethanol labelled with deuterium is used, the deuterium appears in the reduction product, NADB, of NAD^+ giving (R)-configuration.



NAD^+ NADD

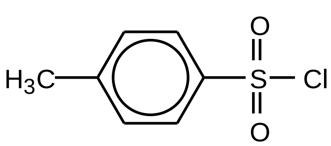
Dehydrogenases catalyse also the opposite reaction, which like the former is stereospecific.

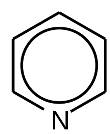


NADD (R)-ethanol-1-d NAD^+

Based on these observations, write equations showing what is happening in the following experiment. Use correct stereochemical representation of all the compounds involved.

CH_3CDO + NADH $\longrightarrow$ alcohol **A** $\xrightarrow[\text{pyridine}]{\text{TsCl}}$ **B** $\xrightarrow{\text{NaOH}}$ **C** $\xrightarrow{NAD^+}$ **D** + **E**

Note: TsCl = 

, and pyridine is 

which acts as a base.