AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART A

1989

<u>Instruction to candidates</u>

(1) You are allowed **10 minutes** to read this paper, and **2 hours** to complete the questions.

(2) You are **not** permitted to refer to books, notes or periodic tables but you may use an 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 <u>black</u>** or **<u>blue</u> ball point pen** for your written answers, pencil or other coloured pens are **not** acceptable.

Question 1

The Earth's oceans contain on average about 10^{-9} M dissolved cadmium(II), an element which is very toxic to many forms of marine and terrestrial (and extra-terrestrial??) life.

As well as 'uncomplexed' Cd^{2+} (really a complex with H_2O), it is thought that the likely complexes to be formed by cadmium(II) in seawater are $CdOH^+$, $CdCO_3$ and a series of chloro-complexes: $CdCl^+$, $CdCl_2$ and $CdCl_3^-$.

The **stepwise** equilibrium constants (stability constants) at 25°C for the **formation** of these complexes are:

log K($CdOH^+$) = 5.8
log K($CdCO_3$) = 4.0
log K($CdCl^+$) = 1.46
log K($CdCl_2$) = 0.78

$\log K(CdCl_3^-) = 0.07$

For convenience, we write the **total** concentration of dissolved carbon dioxide as C_T and the **total** concentration of cadmium(II) as Cd_T.

At 25°C, the average pH of seawater is 8.0, the chloride concentration is 0.55M, $C_T = 10^{-2.3}$ M and $Cd_T = 10^{-9}$ M. The acid dissociation constants of "carbonic acid" in seawater are $pK_{a1} = 6.37$ and $pK_{a2} = 10.33$, and $pK_W = 13.7$ in seawater at 25°C.

(a) Derive an **expression** for the concentration of CO_3^{2-} in seawater in terms of $[H^+]$, C_T and appropriate equilibrium constants. You do not need to numerically evaluate your expression.

(b) Derive an **expression** for the concentration of $CdOH^+$ in seawater in terms of $[H^+]$, $[Cd^{2+}]$ and appropriate equilibrium constants. You do **not** need to numerically evaluate your expression.

(c) Derive an **expression** for the concentration of $CdCO_3$ in seawater in terms of $[H^+]$, $[Cd^{2+}]$, C_T and appropriate equilibrium constants. You do **not** need to numerically evaluate your expression.

(d) Derive **expressions** for the concentrations of each of the **three** chloro-complexes in seawater in terms of $[Cl^-]$, $[Cd^{2+}]$ and appropriate equilibrium constants. You do **not need** to numerically evaluate your expressions.

(e) Using the mass-balance equation for cadmium, show that only 0.95% of cadmium is uncomplexed in seawater at 25°C.

Question 2

(a) With the aid of clearly labelled diagrams illustrate the orbitals and hybrid orbitals used to account for the shapes and bonding in any three of the following:

(i) BF_3 (ii) SeF_6 (iii) SF_4 (iv) C_6H_6 (v) NO_2^-

(b) Using the molecular orbital model, write electron configurations for the following diatomic species and calculate the bond orders. Which ones are paramagnetic?

(i) H_2^- (ii) CO (iii) NO (iv) O_2^+ (v) N_2^-

(c) How many unpaired electrons do each of the following complex ions have in their ground state configurations? Your answer should include a clearly labelled *d*-orbital splitting diagram for each species.

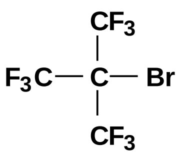
(i) $CoCl_4^{2-}$ (ii) $Co(CN)_6^{4-}$ (iii) $Co(NH_3)_6^{3+}$ (iv) $Co(NH_3)_6^{2+}$ (v) CoF_6^{3-}

(d) Draw and name all the possible linkage, geometric and optical isomers of $[Co(en)_2(SCN)Cl]Cl$.

Question 3

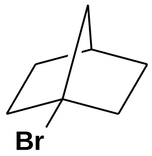
(a) Rather surprisingly 1,2,3-trichlorobenzene is manufactured from aniline by a multistep route, which involves a nitration. Can you suggest the various intermediate compounds in this synthesis and the reagents used in the different steps?

(b) (i) Explain why the bromide **(1)** is unreactive to S_N1 reaction conditions.



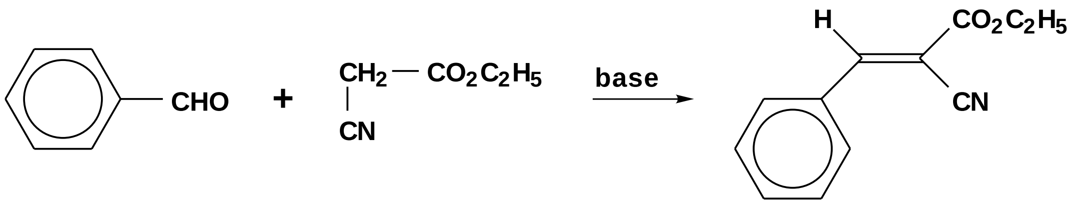
(1)

(ii) Explain why the bromide **(2)** is inert to both S_N1 and S_N2 reactions.

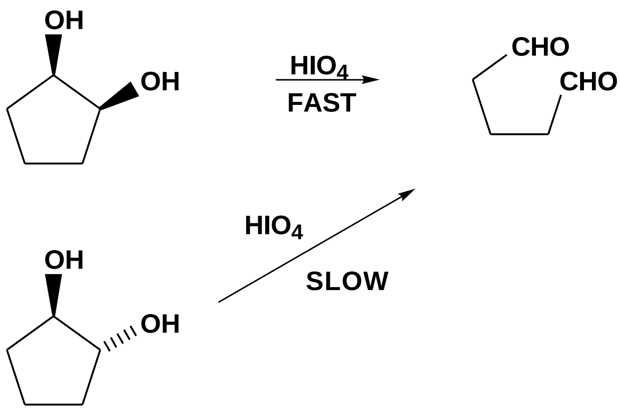


(2)

(c) Suggest a mechanism for the following reaction.



(d) The cleavage of 1,2-diols with periodic acid (HIO_4) is a well known and widely used reaction.
Given the following information.



(i) What can you suggest concerning the structure of the iodine containing intermediate species for this reaction?

(ii) Using carefully drawn Newman projections suggest why (±) 2,3-butandiol reacts faster with periodic acid than *meso*-2,3-butandiol.

Question 4

(a) A 1.00 x 10^{-3} m aqueous solution of acetic acid was found to lower the freezing point of water by 0.0021 K. Determine the degree of ionisation for this acid. Show all working.

Data: cryoscopic constant for acetic acid: 1.86K.kg.mol^{-1}.
Relative atomic masses: C = 12.01; O = 16.00; H = 1.008.

(b) During prohibition in America the grape growers of California had to use their grapes to make syrup rather than wines. Since the grape harvesting season is relatively brief the grape producers preferred to store the grape juice while harvesting and concentrate it for syrup later. In order to prevent fermentation of the grape juice it was common practice to saturate the juice with SO_2 (about 1.5kg SO_2 per m^3 of juice) which could then be removed prior to concentration. One technique for removal of the SO_2 was to create a partial vacuum over the juice. Assuming that the rate of removal of SO_2 is proportional to the amount left in the grape juice, and that 50% of the SO_2 was removed in the first half hour of evacuation, calculate how long it took for the SO_2 concentration to be reduced to 75g per m^3 of juice. Show derivations for all equations used.

Data: Relative atomic masses: C = 12.01; O = 16.00; H = 1.008.