FINAL PAPER

PART A

1988

Instruction to candidates

(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.

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

Question 1

(a): Methylmercury(II) cation, CH_3Hg^+, is the 'heavy' metal cation responsible for the toxicity episodes at Minamata, Japan, and elsewhere during the 1960s and 1970s.

Its chemistry is relatively simple. In aqueous solution, the CH_3Hg^+(aq) cation is acidic, losing a proton to form a hydroxy complex:

$$CH_3Hg^+ + H_2O \rightleftharpoons CH_3HgOH + H^+ \qquad \log K_1 = \text{-}4.607$$

The cation can further react with CH_3HgOH to form a binuclear species:

$$2CH_3Hg^+ + H_2O \rightleftharpoons (CH_3Hg)_2OH^+ + H^+ \qquad \log K_2 = \text{-}2.234$$
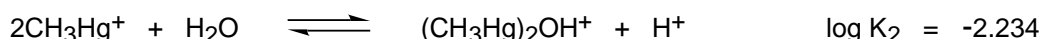
In poisoned humans, methylmercury(II) is found primarily inside red blood cells, where its concentration (in all forms) is approximately 10^{-6}M.

Assuming that a red blood cell contains only water at pH 7.4 (a little simplistic!), calculate the <u>proportions</u> of the three methylmercury(II) species present.

(b): Of course a red blood cell is somewhat more complicated than just described, but as far as a CH_3Hg^+ cation is concerned, apart from water, the only other small complexing agents with significant concentrations are chloride (0.154M) and the tripeptide glutathione (0.002M).

Glutathione is a tetraprotic acid with pK$_a$s of 2.12, 3.53, 8.66 and 9.62 at the ionic strength of a blood cell. The structure of the fully protonated form of glutathione (GS-H$_4^+$) is shown below:
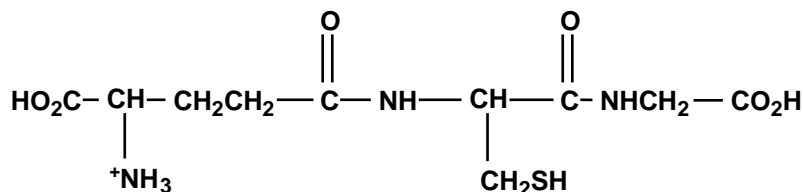

Draw the structures of:

(i) fully <u>de</u>protonated glutathione (the form which exists in aqueous solution at pH 12).

(ii) the major form or forms of glutathione at a physiological pH of 7.4.

(c): The equilibrium constants for the formation of methylmercury(II) complexes with chloride and with the fully deprotonated form of glutathione (GS) are:

$$CH_3Hg^+ \ + \ Cl^- \quad \rightleftharpoons \quad CH_3HgCl \qquad \log K_3 \ = \ 4.90$$

and $\quad CH_3Hg^+ \ + \ GS \quad \rightleftharpoons \quad CH_3HgSG \qquad \log K_4 \ = \ 16.00$

Draw the structures of the methylmercury(II) species present in a red blood cell at pH 7.4, in order of their <u>decreasing</u> abundance. Consider water, chloride and glutathione as the only potential complexing agents.

Question 2

(a): Using benzene together with <u>one</u> other aromatic molecule of your choice and any inorganic reagents you wish, suggest a synthesis for
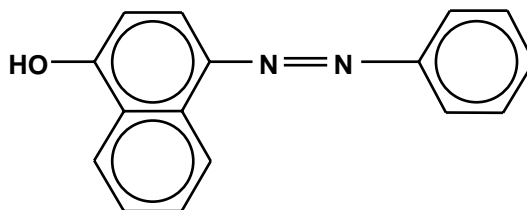
b): *cis*-2-Phenylcyclohexyl-*p*-toluenesulfonate (1) reacts with the strong base potassium *tert*-butoxide in *tert*-butyl alcohol at 50°C to give exclusively 1-phenylcyclohexene (2). *trans*-2-Phenylcyclohexyl-*p*-toluenesulfonate (3) does not give any of the alkene under the same conditions. Draw clear structures for the compounds (1) to (3) and explain the observations.

[Note: *tert*-butyl alcohol is alternatively named 2-methylpropan-2-ol]

(c) An aliphatic compound **A** is a very useful solvent and an industrial reagent. It contains 66.7% C, 11.1% H, and 22.2% O. Upon reduction of **A** a secondary alcohol **B** is formed. It contains 64.9% C, 13.5% H, and 21.6% O. A compound **C** is prepared from bromoethane with magnesium in dry ether. When the product of the reaction between **A** and **C** is hydrolysed a compound **D** containing 70.6% C, 13.7% H, and 15.7% O is formed.

[Relative atomic masses: C = 12.01   H = 1.00   O = 16.00]

(i) Give the empirical formulae of **A, B** and **D**.

(ii) Deduce the molecular and structural formulae for **A** to **D**. Give your reasoning. How would you verify your deductions?

(d): 4-Nitrophenol is a stronger acid than phenol itself. Using arguments based on mesomeric and inductive effects provide a rationalization for the observed facts.

Question 3.

(a) Write electronic configurations for each of the following species. How many unpaired electrons does each have in the ground state?

(i) P   (ii) O^+ (iii) Cr   (iv) Mn   (v) Co^{3+}

(b) For any <u>three</u> of the following molecules, draw the Lewis structure (including resonance structures where applicable), predict the molecular structure and describe the bonding (in terms of hybrid orbitals).

(i) BCl_3 (ii) O_3 (iii) NO_2^- (iv) $XeOF_4$ (v) OCN^-

(c) For each of the following classical coordination compounds name and draw all the possible geometric and optical isomers. [en = $H_2NCH_2CH_2NH_2$]

(i) $Pt(NH_3)_2(SCN)_2$ (ii) $[Cr(en)(NH_3)_2I_2]I$
(iii) $K[Co(C_2O_4)_2(H_2O)_2]$

(d) The d^6 Co^{3+} complex ions CoF_6^{3-} and $Co(NH_3)_6^{3+}$ are different in colour and have different magnetic properties. Explain these differences using the crystal field model.

Question 4.

(a) A forensic chemist is given a white solid that is suspected of being pure cocaine ($C_{17}H_{21}NO_4$, mol. wt. = 303.35). She dissolves 1.22 ± 0.01 g of the solid in 15.60 ± 0.01 g of benzene. The freezing point was lowered by $1.32 \pm 0.04°C$.

[Freezing point of benzene = 5.5°C; $K_f = 5.12°C.kg.mol^{-1}$]

(i)   What is the molecular weight of the substance? Assuming that the percentage uncertainty in the calculated molecular weight is the same as the percentage uncertainty in the temperature change, calculate the uncertainty in the molecular weight.

(ii)   Could the chemist unequivocally state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine ($C_{19}H_{21}NO_3$, mol.wt. 299.36)?

(b): Consider the following galvanic cell:

Pb | Pb^{2+}(0.10M) || VO^{2+}(0.10M), V^{3+}(10^{-5}M), pH = 1.00 | Pt
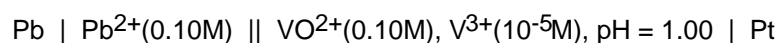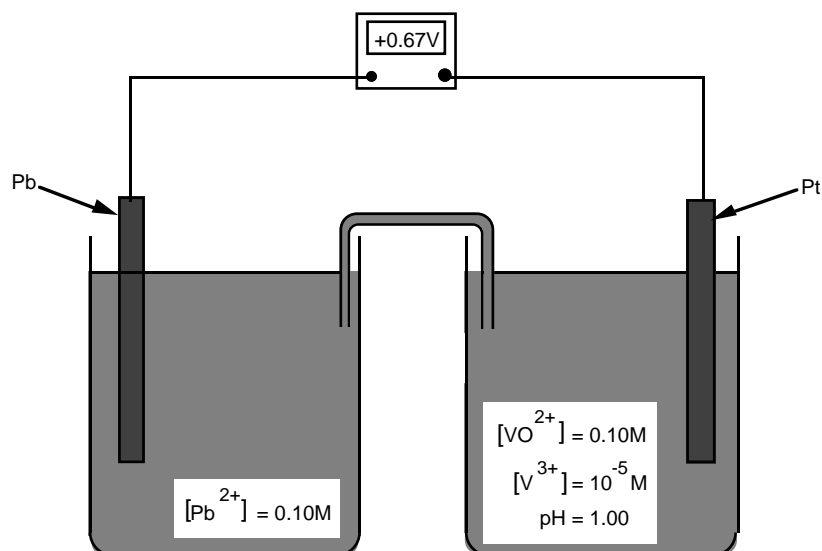
At 25°C the measured cell potential is +0.67 V.

(i) Calculate the standard reduction potential (E°) for the Pb/Pb^{2+} couple at 25°C, given that E° for the VO^{2+}/V^{3+} couple is +0.39V at 25°C.

(ii): Because we now know E°(Pb/Pb^{2+}), we can use a lead electrode as an analytical tool to measure the concentration of Pb^{2+} ions in a sample of polluted mine water.

Our analytical tool will be the galvanic cell containing lead and hydrogen electrodes:

Pb | water sample containing Pb^{2+}, pH = 2.00 | H$_2$(g), Pt
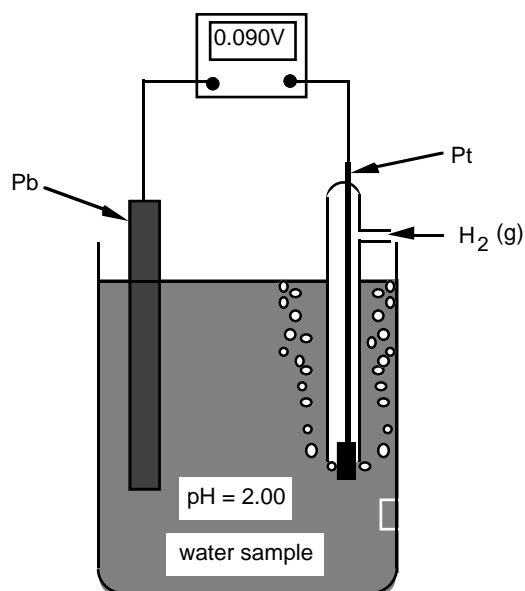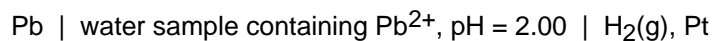
The measured potential of this analytical cell is +0.090 V when the partial pressure of H$_2$ is 1.00 atm. What is the concentration of Pb^{2+} in the mine water?

[Nernst Eqn.: $E = E° - \dfrac{0.0592}{n} \ln Q$]