AUSTRALIAN CHEMISTRY OLYMPIAD

FINAL PAPER

PART B

1989

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 an electronic calculator and molecular models.

(3)   You must attempt **all** questions, so be sure to allocate your time appropriately.

(4)   Answers must be written in the blank space provided immediately below each question in the exam booklet. Rough working must be on the back of pages.

(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

A white crystalline ionic solid **A**, because of its thermal instability, is used extensively as a direct explosive in mining and quarrying operations. At high temperatures (>300 °C) it can explode violently giving off two colourless and odourless gases **B** and **C** and H_2O. Under controlled thermolysis at about 250 °C, a gas **D** is liberated with H_2O also as a by-product. **D** is a moderately unreactive gas comprised of linear unsymmetrical molecules, as expected for a 16-electron triatomic species. Like **A**, **D** is also thermodynamically unstable and decomposes exothermically upon heating to give **B** and **C**. With atomic oxygen, **D** gives **E** which exists in equilibrium with **F**, which is paramagnetic. At high pressures and moderate temperatures **F** rapidly disproportionates to **D** and a brown gas **G**. In the presence of **C**, **F** is also quickly converted to **G**, which exists in equilibrium with colourless **H**. In a medium of high dielectric constant such as nitromethane, **H** undergoes a self-ionization equilibrium with **I** and **J**. **I** is isoelectronic with CO and **J** is the anionic constituent of **A**. **H** can be oxidised by ozone to give a highly deliquescent light sensitive solid **K**. X-ray diffraction studies show that solid **K** consists of an ionic array of linear **L** and planar **J**. In the gas and solution state, **K** is probably molecular, **L** is isoelectronic with CO_2.

Identify all the lettered compounds and write down all the equations described.
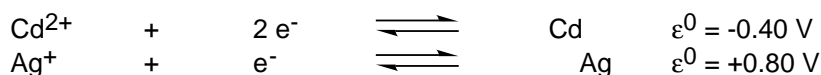
Question 2

After attending a Chemistry Olympiad Summer School, an enterprising and environmentally aware student from a mining town decided that it should be possible to measure the concentration of cadmium in the city's river water if the following experimental apparatus was used.
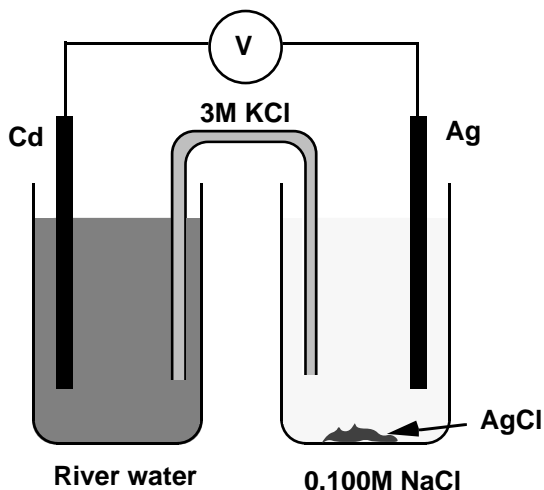
The student intended to fill the right-hand beaker with 0.100M NaCl solution and the left-hand beaker with river water and then to measure the cell potential with a very high resistance voltmeter. Knowing the cell potential, she figured that it ought to be a simple matter to calculate $[Cd^{2+}]$ in the river-water using Nernst's equation.

Conveniently, the temperature of the cell components and river water was 25°C. Her trusty 2nd edition of Zumdahl told her that useful standard reduction potentials at 25°C were:

$$Cd^{2+} \quad + \quad 2\,e^- \quad \rightleftharpoons \quad Cd \qquad \varepsilon^0 = -0.40 \text{ V}$$
$$Ag^+ \quad + \quad e^- \quad \rightleftharpoons \quad Ag \qquad \varepsilon^0 = +0.80 \text{ V}$$

and that $K_{sp}(AgCl) = 1.6 \times 10^{-10} \text{ M}^2$.

Data: $F = 96{,}485 \text{ Cmol}^{-1}$; $\qquad R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$.

(a) Write an expression which allows you to calculate $[Cd^{2+}]$ from the potential of the electrochemical cell which is set up in the apparatus.

(b) If the measured cell potential was +0.90 V, what was the concentration of cadmium in the river water?

(c) The student was so enthused by the success of this experiment (she might be able to sell the idea??) that she wondered whether the same setup could be used to measure the cadmium concentration in seawater.

In fact she wondered if the same cell potential would be obtained when the left-hand beaker contained seawater with the same total concentration of cadmium as the river water?

Being an experimentalist rather than a theorist, she decided to test her suspicions by adding just enough NaCl to the river water in the cell to make the chloride concentration identical to seawater, 0.55M.

What cell potential did she measure?

Data: In seawater only 0.95% of cadmium is uncomplexed and the major complexes are the chloro complexes. You can ignore the concentrations of hydroxy and carbonato complexes.

(d)   The student noted that the cell potential (for the particular sample of river water in part (b)) changed from 0.90V in the morning when the ambient temperature was 25°C, to 0.95V in the afternoon when the temperature had risen to 35°C.

Is the equilibrium

$$2\,Ag^+ + Cd \rightleftharpoons Cd^{2+} + 2\,Ag$$
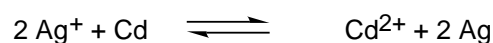
exothermic or endothermic? Explain your answer.

You can assume that the solubility of silver chloride does not change from 25°C to 35°C.

(e)   Explain why it is better to have 0.1M NaCl and some solid AgCl in the right-hand beaker, rather than 0.1M $AgNO_3$. Why is the AgCl necessary?

Question 3

The industrial conversion of an organic compound **X** to its isomer **Y** is carried out at constant temperature and pressure by passing **X** at 5 $cm.s^{-1}$ down a reactor tube packed with catalyst. The gas flows smoothly through the tube without any back mixing and its composition at any distance along the tube is uniform across the tube. The table below gives the gas analyses at various distances along the pipe.

Distance (cm)	% Y
0	0.0
25	5.0
50	9.5
100	18.2
170	28.9
290	44.1
400	55.2

a)   Assuming that the rate of the backward reaction is much less than the forward reaction show the reaction order in **X**.

b)   For the process to operate economically, 80% of **X** should be converted to **Y**. How long should the reactor tube be made;

i)   using the data given above;
ii) if the flow rate is halved;
iii) if a new catalyst is discovered which exactly doubles the rate constant ?

c)   Steam pipes are available for heating 3 metres of the reactor tube. Which 3 metres should be so heated ? Explain you answer briefly.

Question 4

Simple chemical tests were once the backbone of structure determination in organic chemistry. For instance the reaction of a molecule with "sodium hypoiodite" ($NaOH/I_2$ in water) to yield a pale yellow precipitate of iodoform (CHI_3) was a test for a methyl ketone or a group easily oxidised to a methyl ketone. The following problem is an example of a classical structure determination based on simple chemistry.

The toxic principal in buttercups is an unstable oil called protoanemonin, $C_5H_4O_2$, which is readily hydrolysed by acid or base to **A,** $C_5H_6O_3$. Unlike protoanemonin, **A** dissolves with effervescence in sodium bicarbonate solution and can be converted to a 2,4-dinitrophenylhydrazone. On treatment with hydrogen in the presence of platinum, protoanemonin gives **B**, $C_5H_8O_2$. **B** does not dissolve in sodium bicarbonate solution but does so in sodium hydroxide solution; acidification of this solution gives an acid **C**, $C_5H_{10}O_3$, which on standing reverts to **B**. When **C** is treated with sodium hydroxide and iodine, it gives iodoform (triiodomethane) and **D**, $C_4H_6O_4$. **D** evolves a gas from sodium bicarbonate solution. **D** also reacts with aqueous sodium hydroxide, 147.5mg

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of **D** being required to neutralise 10mL of 0.125M barium hydroxide. **D** can be obtained by treating 1,3-cyclohexadiene with KMnO$_4$ under vigorous conditions.

Explain the above reactions and deduce a probable structure for protoanemonin.

Data: Relative atomic masses: C = 12.01;   O = 16.00;   H = 1.008;   Ba = 137.3.