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## RIO TINTO AUSTRALIAN CHEMISTRY OLYMPIAD

### FINAL EXAMINATION — PART A

1999

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 6 to 8.

#### Instructions to candidate

- (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 non programmable electronic calculator.
- (3) Questions 1, 2, 3, 4 and 5 must be attempted. In the organic section you must answer questions 6 and 7, and any two of questions 8, 9 and 10. A guide for time allocation is supplied at the beginning of each question.
- (4) Data is supplied, where necessary, with each question.
- (5) Answers **must** provide **clearly laid out working** and **sufficient explanation** to show how you reached your conclusions.
- (6) 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.
- (7) Ensure that your name is written in the appropriate place on **each page** of your examination booklet.
- (8) Use **only black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

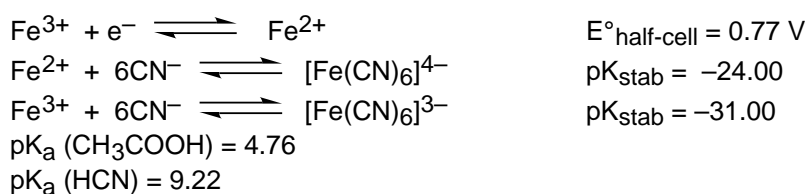
#### Question 1 (45 minutes)

**Note:** Data for this question can be found at the end of the question.

- a) In solving equilibrium problems, one often makes use of various assumptions to simplify the expressions involved. It is often interesting to investigate the circumstances under which these assumptions hold, and what errors they produce. Consider the weak acid, HA.
  - (i) Assuming that the effect of water dissociation can be ignored, and the fact that HA is a weak acid, derive a simple expression relating the hydrogen ion concentration in a solution containing HA, to the concentration of HA and the value of  $K_a$  for HA. You may assume that the dissociation of HA itself has little effect on [HA] in the solution.
  - (ii) Construct a similar relationship if one considers the effect of acid dissociation on the concentration of HA in solution.

- (iii) Using your answers to (i) and (ii) above, estimate the  $pK_a$  of the acid HA, given that a 2.0% error is introduced in neglecting the effect considered in (ii) when calculating the hydrogen ion concentration in a 1.0 M HA solution.
- b) A 1.0 L solution, containing both  $Fe^{2+}$  and  $Fe^{3+}$  ions has a half-cell potential of 0.469 V. The total mass of iron in the solution is 0.838 g.
- (i) Calculate the concentration of  $Fe^{3+}$  in the solution.
- 0.10 moles of KCN were added to the solution. You may assume that no substantial change in volume occurred. The system was allowed to come to equilibrium.
- (ii) Explain why the concentration of  $[Fe(CN)_6]^{3-}$  is approximately equal to the concentration of  $Fe^{3+}$  calculated in part (i).
- (iii) Hence, or otherwise, calculate the equilibrium concentrations of:
- (A)  $[Fe(CN)_6]^{4-}$   
 (B)  $Fe^{2+}$   
 (C)  $Fe^{3+}$
- (iv) What is the value of Q, the reaction quotient for the equilibrium  $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ ?
- (v) Calculate the new potential for this half-cell at 298 K.
- c) Vinegar can be considered as a crude ethanoic acid solution. However, since ethanoic acid is a weak acid, it is likely that vinegar also contains reasonable concentrations of the ethanoate ion. The pH of household vinegar is about 2.15.
- (i) Calculate the concentrations of ethanoic acid and ethanoate ion in a bottle of vinegar
- (ii) Use the Henderson-Hasselbalch equation, or another suitable method, to calculate the number of moles of hydroxide ion that need to be added to 1.00 L of vinegar to increase the pH by 1 pH unit. Neglect any changes in volume.
- (iii) If the number of moles of hydroxide ion calculated in part (ii) were added to 1.00 L of pure water, what would be the pH change observed?
- (iv) Explain why hydroxide ion has less of an effect on the pH of vinegar than the pH of pure water. Appropriate diagrams may be helpful in your answer.

**DATA:** (all at 298 K)



**Question 2 (25 minutes)**

- a) Arrange each of the following complex ions in order of increasing stability and explain your choice:  $[Co(H_2O)_6]^{2+}$ ,  $[Mn(H_2O)_6]^{2+}$ ,  $[Cu(H_2O)_6]^{2+}$ ,  $[Ni(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{2+}$ . [Support your answer with appropriate d orbital splitting diagrams.]
- b) Would you expect the analogous tris(ethylenediamine) complexes to be more or less stable than their hexaaqua counterparts? Explain.
- c) How many stereoisomers would you expect for the tris(ethylenediamine)chromium(III) cation? Sketch them. Would you expect a similar number of stereoisomers for the complex ions

$[\text{Cr}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)(\text{en})_2]^{3+}$  and  $[\text{Cr}\{\text{(S)-H}_2\text{NCHMeCH}_2\text{NH}_2\}_3]^{3+}$ ? Explain. Can you suggest systematic names for the latter two cations?

### Question 3 (20 minutes)

**Note:** Data for this question can be found at the end of the question.

- Explain the formation of the so-called "spectral lines" in atomic emission spectra.
- The frequencies of the spectral lines in the hydrogen atomic emission spectrum were found to fit the equation below. What can be deduced from this experimental finding?

$$\nu = \frac{R_H}{h} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

- Calculate the ionisation energy for a hydrogen atom in its ground state.
- The Bohr model for hydrogen atoms describes the atom using a single quantum number  $n$ , however the quantum-mechanical model for hydrogen atoms uses four quantum numbers,  $n$ ,  $l$ ,  $m_l$  and  $s$ . Both models correctly predict the energy levels of a hydrogen atom using only the single quantum number  $n$ . What may be deduced about the other quantum numbers? Does this deduction hold for the quantum-mechanical energy levels in a helium atom? Why/Why not?

**Data:**  $R_H = 2.180 \times 10^{-18} \text{ J}$   
 $h = 6.626 \times 10^{-34} \text{ J s}$   
 $n_1$  and  $n_2$  are integers

### Question 4 (20 minutes)

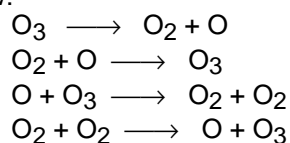
- If a chemical system is separated from its surrounds by an adiabatic barrier, how may the state of that system be changed?
- At the triple point of water, the temperature and pressure are such that the solid, liquid and gaseous phases for water coexist indefinitely. Describe the processes that are occurring and the chemical potentials of the phases present.
- Define the enthalpy change associated with a process (an equation is not sufficient) and derive an expression for the enthalpy change at constant pressure and temperature for a reaction that consumes a gas.

### Question 5 (25 minutes)

- Ozone is an unstable allotrope of oxygen, so much so that it decomposes explosively if compressed. At atmospheric pressure the decomposition is slow enough that ordinary spectroscopy can be used to follow the conversion into di-oxygen and the following rate law has been measured;

$$\text{rate of consumption of } \text{O}_3 = k[\text{O}_3]^2/[\text{O}_2]$$

One possible set of simple, single steps can be proposed to account for this experimental rate law:



The first two steps are known to be fast and the third step seems much slower in comparison. The fourth step is clearly very, very slow. Derive the rate law, and check it against the experimentally determined rate law.

- b) Often two reactants can combine in different ways to give two different sets of products. Usually only one set of products is desirable, the others being considered as 'side products' and have to be separated afterwards. Consider the two possible reaction schemes;



And,



The first scheme actually proceeds via a step where *A* slowly fragments into *C* and *G*, where upon *G* quickly reacts with *B* to give *D*. The second scheme is a second order process which gives *E* and *F* directly.

- (i) What can be done experimentally to favour the second scheme over the first?

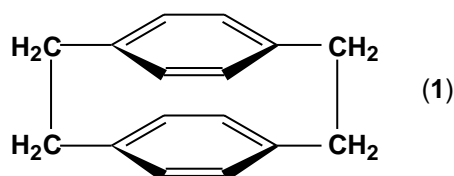
### ORGANIC SECTION (45 minutes)

STUDENTS MUST ANSWER QUESTIONS 6 and 7 TOGETHER WITH ANY TWO OTHER QUESTIONS.

In all questions you can assume a work up with water and adjustment of pH as required.

#### Question 6 (6 minutes)

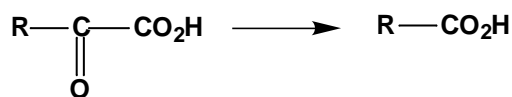
The two benzene rings shown in the structure below of the cyclophane molecule (1) are unable to rotate and as such are held essentially parallel to each other.



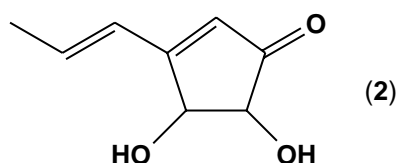
- a) Draw the structures of all the isomers which can be obtained by adding a total of two methyl groups to the aromatic rings of the cyclophane.
- b) Determine which, if any, of the isomers will be optically active (chiral), and explain the reasoning behind your decision.

#### Question 7 (9 minutes)

So called  $\alpha$  keto acids degrade in the presence of hydrogen peroxide to afford the related carboxylic acid, as shown below.



This information was exploited in determining the absolute chemistry of Terrein (2), the planar structure of which is shown below:



Treatment of (2) with ozone followed by reaction of the ozonide with hydrogen peroxide yielded (+) tartaric acid [(2R)(3R)(+)-2,3-dihydroxybutan-1,4-dioic acid].

- a) Using the partial diagram provided in the answer box below complete the Fischer projection of (+) tartaric acid.

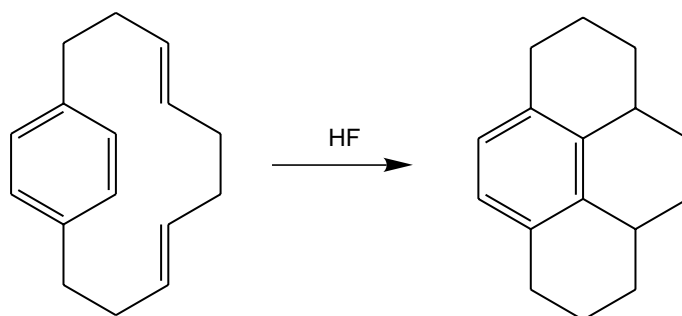


- b) Draw structures for the ozonolysis fragments initially derived from (2) and indicate which of these would on further oxidation with  $\text{H}_2\text{O}_2$  be converted to (+) tartaric acid.
- c) Deduce the correct absolute stereochemistry of (2) and illustrate this with a clear diagram.

**Question 8 (15 minutes)**

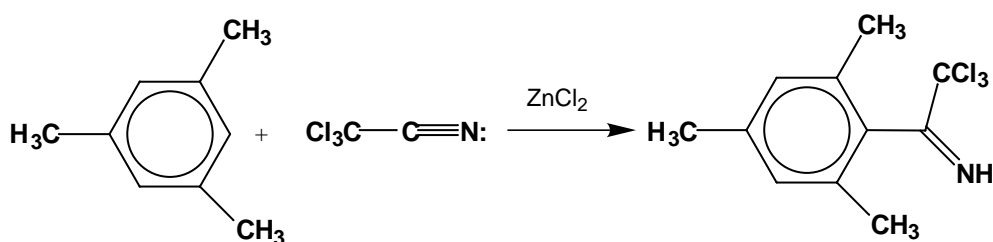
Based upon your knowledge of electrophilic substitution of benzene:

- a) Write a mechanism to account for the following reaction:

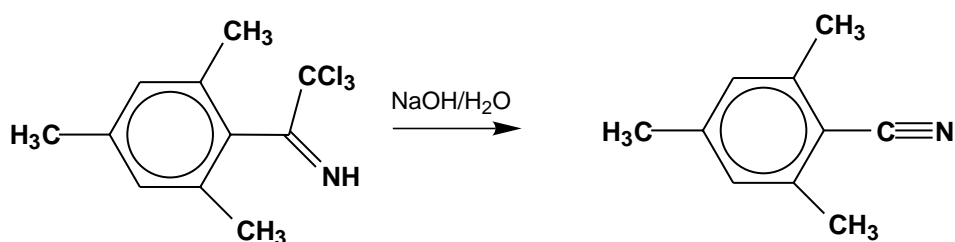


- b) Recalling that some electrophilic substitutions are facilitated by Lewis acids:

Suggest a reasonable mechanism for the following reaction:



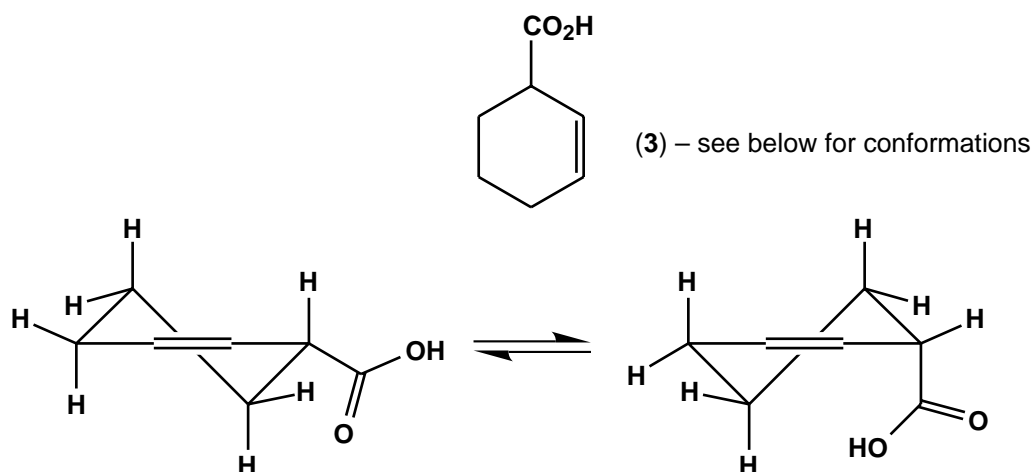
- c) The product of the reaction in part (b) undergoes a reaction reminiscent of the iodoform reaction.



Can you suggest a mechanism for this reaction?

**Question 9 (15 minutes)**

Cyclohex-2-ene-1-carboxylic acid (3) (see below) reacts with bromine to yield a new compound (4)  $\text{C}_7\text{H}_9\text{O}_2\text{Br}$ .

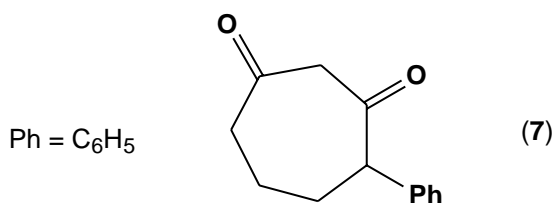


- How many double bond equivalents are present in (4)?
- Why do you think the reaction doesn't simply result in the adding of bromine to (3) to yield  $C_7H_{10}O_2Br_2$ ?
- Suggest two possible regioisomeric structures for the product (4) and deduce which of these is most likely to be correct.
- Suggest a mechanism for the formation of compound (4).
- In a similar fashion cyclohex-3-ene-1-carboxylic acid reacts with bromine to yield a product (5). However (5) unlike (4) readily reacts with base to eliminate HBr.

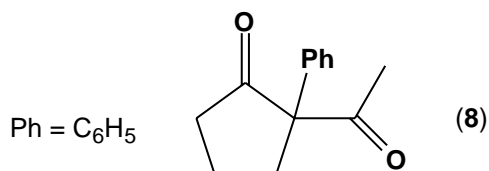
Explain the difference in reactivity of (4) and (5) with base.

### Question 10 (15 minutes)

The base catalysed ( $NaOCH_3/CH_3OH$ ) reaction of methyl 5-phenyl-6-oxoheptanoate (6) was studied as a possible route to the seven membered ring diketone (7).



- Write a structural formula for (6).
- Suggest the mechanism for the formation of (7).
- In practice no (7) was formed but rather the five membered ring product (8) was isolated.



Outline with a mechanism the formation of (8).

- Suggest why (8) rather than (7) was formed in the reaction.