RIO TINTO
AUSTRALIAN
SCIENCE
OLYMPIADS

FINAL SELECTION EXAMINATION for the 2004 AUSTRALIAN CHEMISTRY OLYMPIAD TEAM

PART A

2003

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 Student

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. All questions to be attempted. 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 **ALL of the pages** in this examination booklet.

8. Use only **black** or **blue pen** for your written answers, **pencil or other coloured pens are not acceptable**.

Supervisor Declaration

I certify that the final selection examination was carried out under strict examination conditions and that no improper actions occurred during the examination period.

Name of Exam Supervisor: ***(please print)*** …………………………………………………………………..……

Signed: ……………………………………………………………… Date: ……………………………

Please use the enclosed pre-addressed Express Post Envelope to return the Examination.
(Mr R W Switzer, RTASO Chemistry program, PO Box 589, Mudgeeraba QLD 4213).

EXAMINATIONS MUST BE RECEIVED BY
FRIDAY 19th MARCH 2004.

Question 1 (20 minutes)

Data*:*

R_H	Rydberg constant for hydrogen	1.097	x	10^{7} m^{-1}
$-e$	Electron charge	–1.602	x	10^{-19} C
h	Planck's constant	6.626	x	10^{-34} J s
c	Speed of light in vacuum	2.998	x	10^{8} m s^{-1}

(a) Photoelectron spectroscopy (PES) is a useful technique, closely related to the photoelectric effect, for investigating the energy levels of atoms. Monochromatic light is beamed into a gaseous sample of the relevant species, where the photons collide with molecules, knocking electrons from their orbitals. The kinetic energy of the photoelectrons emerging from the apparatus is measured, and the number of electrons is plotted against their energy. Since the kinetic energy of such an electron will be equal to the energy of the incident photon minus the energy needed to remove the electron from the molecule, the energies of the photoelectrons reflect the energies of the orbitals from which they were removed. Thus the photoelectron spectrum will display a peak for each occupied orbital in the system being investigated.

(i) The photoelectron spectrum of helium gas was taken using UV radiation of wavelength 40.0 nm, and a single peak was observed at 6.4 eV. Use the Bohr model to calculate the effective nuclear charge "seen" by the electrons in helium.

(ii) The photoelectron spectrum of neon gas (with X-rays of wavelength 1 nm), on the other hand, displays three peaks, at 372, 1191 and 1218 eV. To which orbital does each of these peaks correspond? Explain your reasoning by sketching the radial probability densities of the relevant orbitals on the same axes. Can you predict the ratio of the intensities (heights) of these three peaks?

(b) The CN molecule has an absorption band in the near-infrared region due to an electronic transition, while the CN^- ion does not absorb in the near-infrared. Draw a labelled MO energy-level diagram for the valence orbitals of both species, and hence:

(i) calculate their bond orders;

(ii) predict their magnetic properties (diamagnetic or paramagnetic); and

(iii) explain the above observation.

Question 2 (25 minutes)

(a) Write ground state valence electron configurations for each of the following species: In^+, Sr^{2+}, V^{2+}, Se^{4+} and Au^{3+}.

(b) For each of the following species draw the Lewis structure and predict the electron pair geometry and molecular shape: $GaBr_3$, $Te(CH_3)_4$ and H_2SeO_3. What is the hybridisation of the central atom in each of these species? Which of these species would be expected to have a dipole moment?

(c) Name the following coordination compounds: $[Cr(H_2O)_6](ClO_4)_2$, $Rb_3[Co(CN)_2(C_2O_4)_2]$ and $[Pt(dmen)(RS\text{-}btn)](PF_6)_2$ (where dmen = $H_2NCH_2CH_2N(CH_3)_2$ and btn = $H_2NCH(CH_3)CH(CH_3)NH_2$]. Which, if any, of these complexes would be expected to exist in stereoisomeric forms? Sketch them. For each of the transition metal ions in these complexes construct a clearly labeled d-orbital splitting diagram and calculate the crystal field stabilization energy in terms of Δ_o.

Question 3 (45 minutes)

(a) An important biological buffer in our body is the HCO_3^-/H_2CO_3 system. It is important in the maintenance of biological pH within a narrow range. The mechanisms of regulation are quite complex but can be simplified to two equations. The first is the equilibration of aqueous H_2CO_3 with gaseous CO_2 in the lung (catalysed by the enzyme carbonic anhydrase). Thus by controlling the breathing rate, and hence P_{CO_2}, the amount of H_2CO_3 in the blood can be adjusted.

$$CO_2\,(g) + H_2O\,(l) \rightleftharpoons H_2CO_3\,(aq) \qquad K = 0.034\ \text{mol L}^{-1}\text{atm}^{-1}$$

The second site of regulation is the kidney. H_2CO_3 in turn equilibrates with HCO_3^- in the blood. The kidney can generate HCO_3^- from or excrete H^+ into the glomerular ultrafiltrate ("unprocessed urine").

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq) \qquad pK_{a1} = 6.35 \qquad pK_{a2} = 10.33$$

Working in concert, the two organs can maintain blood pH at a steady level of 7.41. If the pH is below this level, the body enters into a state called acidosis. If it is above this level, it is called alkalosis. Over time, the organs can rectify the disturbance (the lung within minutes, the kidney within several days). To classify the acid-base disturbances more clearly the terms "respiratory" and "metabolic" are used to indicate that the defect in regulation originated from the lung or kidney, respectively.

(i) Using ↑ or ↓ to indicate how the values of the following will change in the acid-base disturbances described. Write NC if there is no change:

Type of disturbance	P_{CO_2}	$[HCO_3^-]$	$[H^+]$	**pH**
Respiratory acidosis				
Respiratory alkalosis				
Metabolic acidosis				
Metabolic alkalosis				

(ii) Using the principles of chemical equilibrium, explain the following observations:

1. A patient with terminal kidney failure exhibits deep, rapid breathing.
2. A patient with LONG TERM respiratory problems has a blood pH within normal range.

The composition of DRY exhaled air is 79.00% N_2, 14.00% O_2, 6.00% CO_2 and the rest by inert atmospheric gases. However, exhaled air is saturated with water vapour, which has a partial pressure of 47 mmHg at body temperature (37°C).

(iii) Calculate the partial pressure (in mmHg) of CO_2 in exhaled air saturated with water vapour at 37°C.

(iv) Hence calculate the concentrations of H_2CO_3, HCO_3^- and CO_3^{2-} in blood. You may assume the equilibrium constants do not change significantly with temperature. The conversion factor is 1 atm = 760 mmHg.

As a crude assumption, all of the carbonic acid is dissolved in the extracellular volume (V_{EC}). This consists of two components: the plasma volume (V_P) comprising the liquid component of blood; and the interstitial volume (V_I), the volume of fluid bathing the cells of the body tissues that is not in the circulation.

A certain patient presented to the Emergency department with a 2 hour history of severe vomiting. During that time 0.500 L of gastric fluid was brought up (which maybe considered to be a solution of HCl of pH 2.00). After rehydration (0.500 mL of fluid was given to the patient) a blood pH was taken and it was 7.50.

(v) Assuming that the volume and pH changes only affects the V_{EC}, calculate its value. You may assume the vomitus contained no trace of carbonic acid.

(vi) From your answer in (i), determine the type of acid-base disturbance the patient has.

Calcium is an important electrolyte in the blood due to its role in the regulation of membrane potentials and nerve conduction.

(vii) What should be the free $[Ca^{2+}]$ in the blood of a normal person? K_{sp} of $CaCO_3$ is 3.30×10^{-9} at 37°C.

Actually, the amount of "free" (or ionisable) Ca^{2+} is much higher: 1.30×10^{-3} M. This is due to the presence of complexing agents such as citrate, lactate and phosphate. Like Ca^{2+}, the complexed species are distributed throughout the V_{EC}. In the plasma the Ca^{2+} level is higher still: 2.30×10^{-3} M. This is due to the presence of proteins that bind up Ca^{2+}. However, unlike the small ligands mentioned above, the proteins are confined to the V_P due to their large size.

(viii) Calculate the amount of complexed Ca^{2+}. A_W (Ca) = 40.00 g mol^{-1}

(ix) Given that at any one time there are 900. mg of Ca^{2+} in the V_{EC}, calculate V_P.

The major protein involved in Ca^{2+} transport in the circulation is albumin (M_W = 62000. g mol^{-1}). It has a concentration of 37.0 g / L of plasma.

(x) What is the minimum number of Ca^{2+}–binding sites on albumin?

(xi) If your answer in (ix) is the actual number of Ca^{2+}–binding sites, and Ca^{2+} binds to albumin in an all or none manner (either the sites are fully occupied or not at all), give the expression for K_{stab} between Ca^{2+} and albumin.

(xii) Calculate the value of K_{stab} derived in (xi).

(b) 20.00 mL of 0.01500 M Sn^{2+} in 0.5000 M H_2SO_4 is titrated with 5.000 x 10^{-3} M $Cr_2O_7^{2-}$ at 298 K. Assume complete dissociation of the acid.

$E°$ ($Cr_2O_7^{2-}/Cr^{3+}$) = 1.360 V at 298 K

$R = 8.31451$ J K^{-1} mol^{-1}

$E°$ (Sn^{4+}/Sn^{2+}) = 0.150 V at 298 K

$F = 96485$ C mol^{-1}

(i) Give a balanced equation for the reaction.

(ii) Calculate E° and ΔG° for the reaction.

(iii) An indicating electrode which is connected to the SHE is immersed into the solution to monitor the potential throughout the titration. Construct a titration curve of mL $Cr_2O_7^{2-}$ added versus E. Give your answer to three decimal places.

Volume $Cr_2O_7^{2-}$ added (mL)	E (volts)
5.00	
10.00	
15.00	
19.00	
19.90	
19.99	
20.01	
20.10	
21.00	
25.00	

(iv) What is the value of E at the halfway point?

(v) What volume of $Cr_2O_7^{2-}$ does one need to add so that E = E°($Cr_2O_7^{2-}/Cr^{3+}$)?

(vi) Derive the expression for E at the equivalence point.

(vii) Hence calculate its value.

(viii) Select an appropriate indicator for this titration from the table below. Explain your reasoning.

Indicator	Colour oxidised	Colour reduced	E° at pH = 0.00
Nitroferroin	Pale blue	Red	1.25
Ferroin	Pale blue	Red	1.06
2,2`–bipyridyl iron(II) sulfate	Faint blue	Red	1.02
5,6–dimethylferroin	Pale blue	Red	0.97
N–phenylanthranilic acid	Purple red	Colourless	0.89
4,7–dimethylferroin	Pale blue	Red	0.88
Diphenylaminesulfonic acid	Red-violet	Colourless	0.85
Diphenylbenzidine	Violet	Colourless	0.76
Diphenylamine	Violet	Colourless	0.76
3,3`–dimethylnaphthidine	Purplish-red	Colourless	0.71
Starch-I_3^-, KI	Blue	Colourless	0.53

Methylene blue	Blue	Colourless	0.52

Question 4 (45 minutes)

Data: Atomic weights: H 1.008 g mol^{-1} C 12.0107 g mol^{-1} Cl 35.453 g mol^{-1}

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light = 2.998×10^{8} m s^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Many of the chemical reactions we observe are initiated by a *thermal* pathway, where energy is gained from collisions between molecules. An alternative mechanism is observed in *photochemical* reactions, where absorption of the energy of one photon excites one reactant molecule:

$$A + h\nu \rightarrow A^*$$

Following excitation a number of different paths are available.

(a) In an experiment a flash of light dissociates molecules dissolved in a solvent instantaneously into two identical free radicals:

$$R\text{-}R + h\nu \rightarrow R^{\bullet} + R^{\bullet}$$

(i) Is it possible to predict what the order of the reaction with respect to disappearance of the radicals will be?

(ii) Typical reactions of free radicals are for them to abstract an available H-atom from a solvent (designated SH), or to recombine to form the starting material. Explain how the two processes can be differentiated by considering order of the reaction with respect to $[R^{\bullet}]$.

(iii) In such an experiment the concentration of free radicals, $[R^{\bullet}]$, was found to vary with time, *t*, after the flash as follows:

$[R^{\bullet}]$ (arbitrary unit)	10.0	3.67	1.35	0.49	0.18
t (10^{-6} s)	0	1	2	3	4

What is the order of the reaction with respect to the radical concentration, and what is the value of the observed rate constant? Graph paper is supplied for this question should you require it.

(iv) In a further series of experiments an inert substance is used to dilute the solvent SH which, however, remains in much greater concentration than the radical.

With [SH] = 5 mol L^{-1} the observed rate constant is 0.1×10^{6} s^{-1}; with [SH] = 2 mol L^{-1} it is 0.04×10^{-6} s^{-1}. What is the order of the reaction with respect to the solvent?

(b) The poisonous gas phosgene is photochemically oxidised:

$$2COCl_2\,(g) + O_2\,(g) \xrightarrow{h\nu} 2CO_2\,(g) + 2Cl_2\,(g)$$

The following mechanism is proposed:

$$COCl_2 + h\nu \xrightarrow{k_1} COCl^{\bullet} + Cl^{\bullet}$$

$$COCl^{\bullet} + O_2 \xrightarrow{k_2} CO_2 + ClO^{\bullet}$$

$$COCl_2 + ClO^{\bullet} \xrightarrow{k_3} CO_2 + Cl_2 + Cl^{\bullet}$$

$$COCl^{\bullet} + Cl_2 \xrightarrow{k_4} COCl_2 + Cl^{\bullet}$$

$$Cl^{\bullet} + Cl^{\bullet} + M \xrightarrow{k_5} Cl_2 + M$$

The rate of the first step is found to be proportional to concentration of phosgene and to intensity of incident radiation I_0.

(i) Using the steady state approximation, find an expression for the rate of formation of CO_2.

(ii) Under what conditions will reaction rate be independent of the oxygen concentration?

(c) Phosgene itself can be produced photochemically by oxidation of chloroform, $CHCl_3$, with dissolved oxygen. This is why in the laboratory chloroform is stored in brown glass.

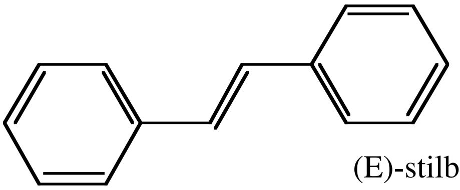
The quantum efficiency of this process (ratio of product molecules produced to absorbed photons) has a value of around 100.

If 1 mg of chloroform is exposed to light of average wavelength 436nm, at an incident intensity of 1.40×10^{-3} J s^{-1}, how long will it take to oxidise completely? You may assume that the liquid absorbs 80.1% of incident radiation.

Organic Section (45 minutes)

Question 5 (15 minutes)

Draw **and name** all products formed when (E)-stilbene (pictured below) is treated with the following reagents. Clearly indicate stereochemical and regiochemical consequences of each reaction.



(E)-stilbene

(a) Cl_2 in H_2O

(b) D_2/Pt

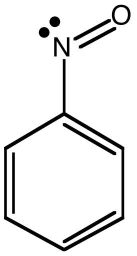
(c) aqueous H_2SO_4

(d) ozone followed by $(CH_3)_2S$

(e) OsO_4 followed by HSO_3^-

Question 6 (10 minutes)

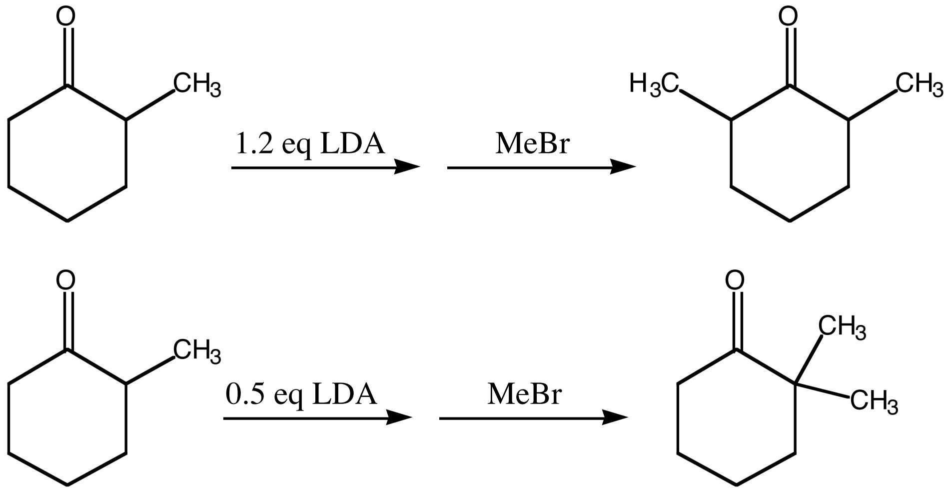
What are the major product(s) when nitrosobenzene (pictured below) is treated with bromine in the presence of $FeBr_3$? Draw resonance structures (Whelan intermediates) to justify your decision. You may assume only the monobromo product is formed.



Question 7 (10 minutes)

When 2-methylcyclohexanone is treated with 1.2 equivalents of lithium diisopropylamide followed by bromomethane, 2,6-dimethylcyclohexanone is formed. However when 2-methylcyclohexanone is treated with 0.5 equivalents of lithium diisopropylamide followed by bromomethane, 2,2-dimethylcyclohexanone is formed.

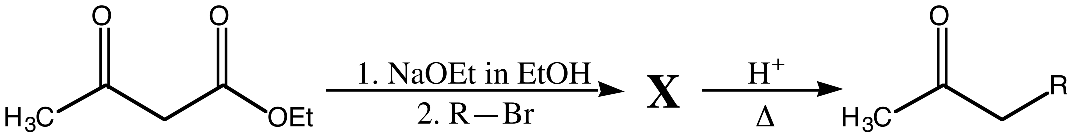
Name:



By considering the intermediates and equilibria involved in these reactions, explain their different regiochemical outcomes.

Question 8 (10 minutes)

The acetoacetic ester synthesis is a series of reactions that give a substituted acetone product starting from an ester of acetoacetic acid (3-oxobutanoic acid). The general reaction scheme is shown below:



(a) Identify product **X** in the reaction scheme above, and give a mechanism for its formation.

(b) Give a mechanism for the formation of the substituted acetone when **X** is heated in acid.