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AUSTRALIAN
SCIENCE
OLYMPIADS

FINAL SELECTION EXAMINATION for the 2003 AUSTRALIAN CHEMISTRY OLYMPIAD TEAM

PART B

2002

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)*** ……………………………………………………………..……

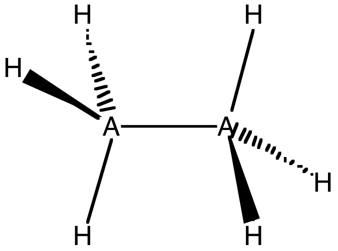
Signed: ……………………………………………………………… Date: ……………………………

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).

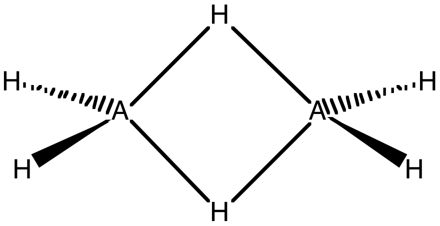
EXAMINATIONS MUST BE RECEIVED BY
FRIDAY 21st MARCH 2003.

Question 1 (20 minutes)

Molecular Orbital (MO) theory can be used to make very precise numerical predictions, but it can also produce surprisingly good qualitative results without any formal calculation at all. This problem involves the use of this theory to make simple predictions about the shape of H_3AAH_3 molecules. Two possible shapes for such a molecule are shown below.



staggered



bridged

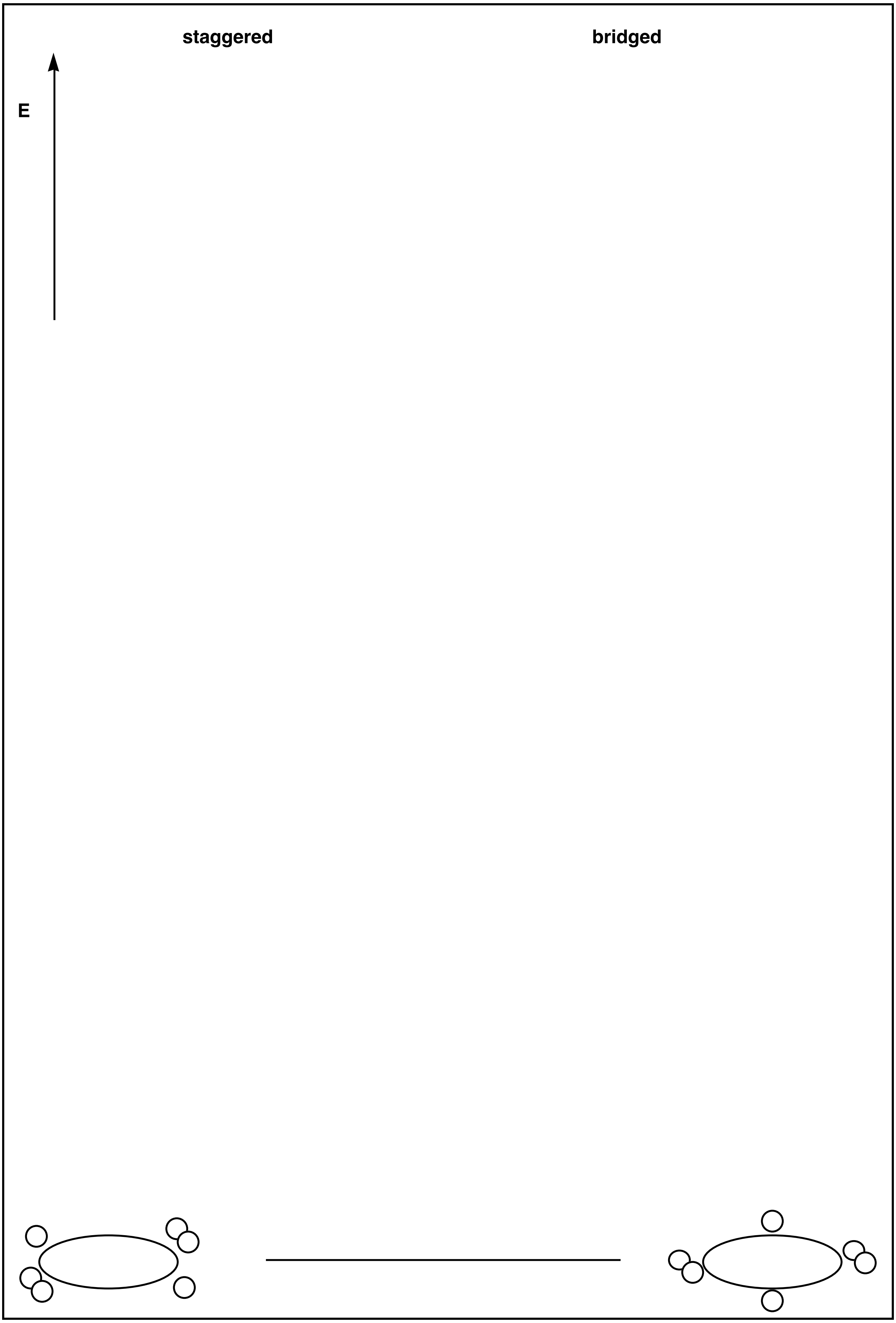
We will consider two well-characterised molecules of this sort: diborane (B_2H_6) and ethane (C_2H_6). To compare the possible shapes for these species, you will need to draw MO diagrams for each shape by following the steps below. To help you get started, parts (a) through to (c) have been completed for the σ_{2s} orbital.

(a) Consider first the homonuclear diatomic molecule A_2. Sketch the 90%-inclusion surfaces of its valence MOs, clearly showing changes in phase, down the left-hand side of the next page in decreasing order of energy. (Note that the σ_{2s} orbital has already been drawn for you.) As there will be no room to draw degenerate orbitals side by side, draw one above the other and connect them by a bracket { to show degeneracy.

(b) We now consider the staggered geometry, allowing each of the MOs drawn in part (a) to mix with the 1s atomic orbitals of suitable H atoms according to the rules of Qualitative Molecular Orbital Theory (QMOT). Add hydrogen 1s AOs to the diagram from part (a) to create molecular orbitals for the complete staggered molecule.

(c) Next, repeat these steps for the bridged structure, drawing the MOs down the right-hand side of the page used for the above and keeping the same approximate energy scale. That is, if a bridged MO is significantly higher in energy than a particular staggered MO, the former should be drawn higher up the page than the latter. Join corresponding MOs (i.e. those based on the same A_2 MO) with lines clearly showing if they have approximately the same energy or if there is a large energy difference between them. (In the example, the MO based on the σ_{2s} orbital has approximately the same energy in the staggered as in the bridged system, as shown by the horizontal line.)

(NB It is correct that there are no answer boxes on this page: parts (a), (b) and (c) are all answered on the large diagram on the next page.)


staggered
bridged
E

(d) Congratulations: you've just drawn a Walsh diagram, which is a qualitative plot of orbital energy against molecular shape. Use this diagram to explain why ethane is staggered while diborane has a bridged shape. Are these species paramagnetic or diamagnetic? (You may wish to number your MOs from the previous page for ease of reference.)

Question 2 (25 minutes)

(a) The doubly charged metal ions of the first row transition elements with the configuration d^1, d^2, … d^9 form mainly octahedral complexes of the general formula $[ML_6]^{2+}$ (L = neutral monodentate ligand). From the magnetic behaviour point of view these complexes are of two types. Those with the same number of unpaired electrons as the $M^{2+}(g)$ ion, the so called "high spin" complexes, and those in which this number is smaller or even zero, the "low spin" ones. If the separation between the energy levels t_{2g} and e_g is Δ and the pairing energy (the energy necessary for two electrons to be coupled into a singlet) is P, predict the ground state electron configuration for these complexes and calculate the energy of stabilization associated with each configuration in terms of Δ and P.

(b) Isomerism is traditionally introduced in Organic Chemistry courses. However, Inorganic Chemistry also offers many different types of isomerism, especially structural. The modern study of coordination compounds began with Alfred Werner[1] and Sophus Mads Jorgensen, more than one hundred years ago. It was their experiments that established the octahedron as the premier structural entity for coordination number six (6) rather than the planar hexagon or the trigonal prism, for example, in the complex ion $[Co(NH_3)_6]^{3+}$. Thus, there are two isomers corresponding to the chemical formula $CoCl_3{\cdot}4NH_3$, the *praseo* and *violeo* complexes. There are also two structural isomers for the complex $[RhCl_3(py)_3]$ (where py = pyridine, C_5H_5N). Rotation of plane polarized light is not limited to organic molecules with a chiral carbon atom. The general condition for optical activity is that the molecule or ion should not possess an improper axis of rotation and the molecule may not possess a center or plane of symmetry. Thus, although there is only one *cis*–$[CoCl_2(NH_3)_4]Cl$ complex, there are two *cis*–$[CoCl_2(en)_2]Cl$ complexes which are enantiomers. ([1] Nobel prize in Chemistry 1913.)

(i) What is the electronic configuration of Co in $[Co(NH_3)_6]^{3+}$?

(ii) What is the type of bonding of NH_3 in $[Co(NH_3)_6]^{3+}$, which is a low spin complex, and of fluoride ion in $[CoF_6]^{3-}$, which is a high spin complex? Place electrons from the ligands in appropriate metal orbitals according to Valence Bond Theory.

(iii) Write the stereochemical formulae and structures for the *praseo* and *violeo* complexes.

(iv) Write the stereochemical formulae and structures for the two $[RhCl_3(py)_3]$ complexes.

(v) How many isomers does the complex with the formula $[Co(en)_3]I_3$ exhibit? How many stereoisomers are possible for the complex $[PtCl_2(NO_2)_2(NH_3)_2]$? Sketch them.

Question 3 (45 minutes)

Do either (a) or (b) in this question.

Either

Data: AW (Bi) = 209.0 g mol^{-1}

(a) The detection limit is one of the basic parameters in quantitative analysis of trace amounts of elements. The detection limit is expressed as the minimal mass of an element which can be determined by a given method with a given accuracy. As an example we shall consider the method used for the determination of microscopic amounts of bismuth. Belcher and co-workers in Birmingham developed a multiplicative method. According to this method a chain of reactions followed by a titration of the final product is carried out. A detailed description follows.

Step 1: To a given small amount of cold acidified solution containing trace amounts of Bi^{3+} excess $K_3[Cr(SCN)_6]$ is added. This leads to quantitative precipitation of bismuth.

(i) Write a balanced net ionic equation of this reaction.

Step 2: The precipitate is filtered off, washed by cold water, and treated with 5 mL of 10% solution of $NaHCO_3$. Upon this treatment the initial precipitate transforms into the precipitate of $((BiO)_2CO_3)$ with formation of $[Cr(SCN)_6]^{3-}$ and H_2O and liberation of CO_2.

(ii) Write a balanced net ionic equation of this reaction (hint: balance the oxygens).

Step 3: To the slightly acidified filtrate transferred to a separating funnel, 0.5 mL of saturated iodine solution in chloroform are added, and the mixture is vigorously shaken. Iodine oxidises the ligand of the complex ion to ICN and sulfate ion.

(iii) Write a balanced net ionic equation of this reaction.

Step 4: After 5 minutes, 4 mL of 2M H_2SO_4 are added to the mixture. The acidification leads to coproportiation (a species oxidised and another species reduced to a common third species) of the iodine species to molecular iodine.

(iv) Write a balanced net ionic equation of the reaction that occurred upon acidification.

Step 5: Iodine is quantitatively extracted by 4 portions of chloroform. The AQUEOUS layer is transferred to a flask, to which 1 mL of bromine water is added, and the mixture is mixed for 5 minutes.

(v) Write the balanced net ionic equations of the reactions that occurred upon the addition of bromine water. Note that an excess of bromine can react with hydrogen cyanide to give BrCN, and iodide is oxidised to IO_3^-.

Step 6: To eliminate an excess of molecular bromine, 3 mL of 90% methanoic acid is added to the mixture, producing Br^- and CO_2.

(vi) Write a balanced net ionic equation of this reaction.

Step 7: To the slightly ACIDIC solution an excess (1.5 g) of KI is added.

(vii) Write the balanced net ionic equations of the reactions that occurred upon the addition of KI. Take into consideration that iodide reacts with BrCN to give molecular iodine and bromide.

Step 8: The resulting solution is titrated by a standard 0.00200 M $Na_2S_2O_3$ solution. The results thus obtained are used to calculate the content of bismuth in the sample taken for analysis.

(viii) How many moles of thiosulfate are equivalent to 1 mol of bismuth in the initial sample?

(ix) What is the minimum mass of bismuth (in μg) which can be determined by this method, given that reliable determination requires no less than 1 mL of standard 0.00200 M $Na_2S_2O_3$ solution?

Or

Data: K_{sp} ($Ag_2C_2O_4$) = 3.50 x 10^{-11} FW ($Ag_2C_2O_4$) = 303.82 g mol^{-1}

$H_2C_2O_4$: pK_{a1} = 1.25, pK_{a2} = 4.27

Ag^+ with NH_3: K_{f1} = 1.59 x 10^3, K_{f2} = 6.76 x 10^3

(b) Two important factors that affect the solubility of a sparingly soluble salt are pH and the presence of a complexing agent. Silver oxalate is one such salt, which has low solubility in water. Its solubility is affected by pH as the anion oxalate reacts with hydronium ions, and also by a complexing agent, such as ammonia, as the silver cation forms complexes with ammonia.

(i) Calculate the solubility (g $100mL^{-1}$) of silver oxalate in acidified water buffered at pH = 5.00.

In the presence of ammonia in aqueous solution, silver ion forms two complexes $[Ag(NH_3)]^+$ and $[Ag(NH_3)_2]^+$.

(ii) What is the solubility (g $100mL^{-1}$) of silver oxalate in an aqueous solution that contains 0.02 M NH_3 at equilibrium and a pH of 10.80?

Question 4 (45 minutes)

Data:

Species(g)	$\Delta_{diss}H^o$ (kJ mol^{-1})
H_2	436
Br_2	193

Species(g)	S^o (J K^{-1} mol^{-1})
H_2	130.58
Br_2	245.18
HBr	198.32

Δ_rH^o**(2)** = +69 kJ mol^{-1}

Δ_rH^o**(3)** = -174 kJ mol^{-1}

$\Delta_{vap}H^o(Br_2)$ = +30.91 kJ mol^{-1}

$T_b(Br_2)$ = 58.7°C

(a) One of the most studied kinetic reaction types has been gas-phase reaction of hydrogen with halogens:

$H_2 + X_2 \longrightarrow 2HX$

The following general radical chain mechanism has been proposed:

Initiation: $H_2 + M \longrightarrow H\bullet + H\bullet + M$ **(1H)**

or $X_2 + M \longrightarrow X\bullet + X\bullet + M$ **(1X)**

Propagation: $X\bullet + H_2 \longrightarrow HX + H\bullet$ **(2)**

$H\bullet + X_2 \longrightarrow HX + X\bullet$ **(3)**

Termination: any of

$H\bullet + H\bullet + M \longrightarrow H_2 + M$ **(4HH)**

$H\bullet + X\bullet + M \longrightarrow HX + M$ **(4HX)**

$X\bullet + X\bullet + M \longrightarrow X_2 + M$ **(4XX)**

Where M is a non-reacting species.

Many of the possible reactions above make no significant contribution and can be legitimately discounted. We will use this fact to develop a solvable mechanism for the reaction.

Although this is a 'general mechanism' the only halogen which appears to conform under normal conditions is bromine. The questions below relate to the system

$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

(i) Which of the alternative initiation steps, **(1H)** or **(1Br)**, will dominate? Explain.

Reactions **(2)** and **(3)** in combination form a catalytic cycle.

(ii) Show this combination and name the species acting as catalyst/s.

Also, at reaction temperature we find that reaction **(2)** has $E_a \approx 80\text{kJ mol}^{-1}$ and reaction **(3)** has $E_a \approx 4\text{kJ mol}^{-1}$, ie **(3)** is far more efficient than **(2)**.

(iii) Find an expression relating $[H\bullet]$ and $[Br\bullet]$. Thus show that $[H\bullet] << [Br\bullet]$ at steady state, assuming $[H_2] = [Br_2]$.

(iv) Which termination step/s is/are relevant, and which can be ignored? Explain.

(v) There is one further complication. Find E_a of the elementary retardation steps

$H\bullet + HBr \longrightarrow H_2 + Br\bullet$ **(-2)**

and $Br\bullet + HBr \longrightarrow Br_2 + H\bullet$ **(-3)**

Will either or both of these play a significant role in the mechanism? Explain.

(vi) Write down your overall simplified mechanism for HBr formation in terms of initiation, propagation, retardation and termination steps, as defined above.

Rearranged, this gives the following proposed mechanism:

(1) $Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br\bullet + Br\bullet + M$ Equilibrium constant = K_1

(2) $Br\bullet + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H\bullet$

(3) $H\bullet + Br_2 \xrightarrow{k_3} HBr + Br\bullet$

(vii) Using the steady state approximation as appropriate, find an expression for the reaction rate for formation of HBr. You may, but need not, assume that step 1 reaches rapid equilibrium. What will the experimental rate law be at the start of the reaction?

(b) Using any of the given data, and assuming that thermodynamic quantities given remain constant over the temperature range considered:

(i) Calculate molar enthalpy of reaction, $\Delta_r H^\circ$, for $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

(ii) Calculate $\Delta_r G^\circ$ of this reaction at 500K.

(iii) Find K_p of the reaction at 500K.

(iv) What is $\Delta_f H^\circ(HBr(g))$?

Organic Section (45 minutes)

Question 5 (8 minutes)

(a) When HBr adds to propene, the major product is 2-bromopropane, the Markovnikov product. Explain why this is the major product, and why little 1-bromopropane is formed.

(b) When HBr adds to 3,3,3-trifluoropropene, however, the anti-Markovnikov product 1-bromo-3,3,3-trifluoropropane is formed. Explain why this is the case?

Question 6 (35 minutes)

A mystery compound **X**, known to give AChO students a sense of euphoria upon discovery of its structure, may be synthesized from benzene as follows:

Benzene is treated with ethanoyl chloride in the presence of $AlCl_3$ to form compound **A**, which when heated with a mixture of concentrated nitric and sulfuric acids forms **B** ($C_8H_7O_3N$). **C** is made by treating **B** with $SnCl_2/HCl$, which upon treatment with ice-cold HNO_2 followed by heating in water gives **D** ($C_8H_8O_2$), which forms a coloured complex with iron(**III**) salts. Treating **D** with aqueous NaOH followed by methyl iodide (iodomethane) gives **E**, which does not give a coloured complex with iron(**III**) salts. When **E** is treated with ethanal and sodium ethoxide in ethanol a mixture of products is formed, amongst them two isomeric products **F1** and **F2** (both $C_{11}H_{14}O_3$). **F1** readily loses water upon heating to give **G** whereas **F2** does not readily lose water. Unlike **F1**, **F2** can be reduced with hydrogen on a palladium catalyst, forming **H**. **F2** can be oxidised to **I** with aqueous sodium dichromate. Treating **I** with sodium ethoxide in ethanol followed by 2-bromoethanol gives **J** ($C_{13}H_{16}O_4$) as the major product. Oxidising **J** with aqueous sodium dichromate gives **K**, which reacts with thionyl chloride ($SOCl_2$) to give **L**. When **L** is heated in the presence of $AlCl_3$ it reacts to form **M** ($C_{13}H_{12}O_4$). Heating **M** with I_2/NaOH forms a yellow precipitate of iodoform and compound **N**, which rapidly decomposes to form a gas **O**, and compound **X**.

Draw out a reaction scheme and identify products **A**-**E**, **F1**, **F2**, **G**-**O** and **X**.

Question 7 (7 minutes)

When pinacol (2,3-dimethylbutane-2,3-diol) is heated with concentrated sulfuric acid, pinacolone (3,3-dimethylbutan-2-one) is formed. Propose a mechanism for this so-called pinacol rearrangement.