AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1987

General instructions.

(1).This paper is in two sections and candidates must answer each section according to the instructions. ie Answer **ALL** questions in section A and **any three** (3) in section B.

(2). All answers must be written in the space provided in the answer book.

(3).Rough working must done on left-hand pages of the answer book.

(4).You are not permitted to refer to books or periodic tables and the only permitted aid is an electronic calculator.

(5) **Make sure your NAME, HOME ADDRESS and HOME TELEPHONE NUMBER are written on the cover sheet .** Your teacher will fill in the other information.

(6). You are permitted **10 minutes** to read the paper followed by **90 minutes** to work the questions.

SECTION A: It is intended that candidates devote not more than 30 minutes to this section. Answer ALL fifteen (15) questions in this section. One choice only is allowed per question and this should be by clearly ticking (√) the chosen answer box in the answer book. If you make a mistake, correct it clearly so that the examiners can read your answer.

Q 1 If the percentage of water of crystallisation in $MgSO_4.xH_2O$ is 13%, what is the value of x?

A , 1
B , 4
C , 5
D , 7.

[Relative atomic masses H =1, O = 16, Mg = 24, S = 32.]

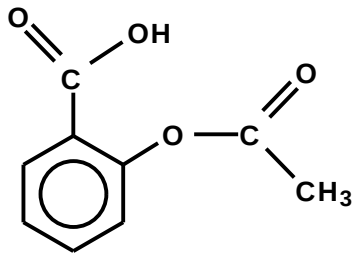
Q 2 Cu^{2+} ions react with Fe^{2+} ions according to the following reaction.

$$Cu^{2+} + 2Fe^{2+} \rightleftharpoons Cu + 2Fe^{3+}$$

At equilibrium, the concentration of Cu^{2+} ions is not changed by the addition of

A , Cu^{2+}
B , Fe^{2+}
C , Cu
D , Fe^{3+}.

Q 3 The most common of all drugs, Aspirin, has the following structure;



The functional groups present in Aspirin make it both

A , a carboxylic acid and an ester
B , an ester and a ketone
C , a carboxylic acid and a ketone
D , a ketone and an alcohol.

Q 4 A hydrocarbon isolated from petroleum has a molecular formula of C_7H_{14}. Which of the following statements is necessarily true?

A , the substance is an alkyne
B , the substance has a branched chain structure
C , the substance is either an alkene or a monocyclic alkane
D , the substance is a linear chain alkane.

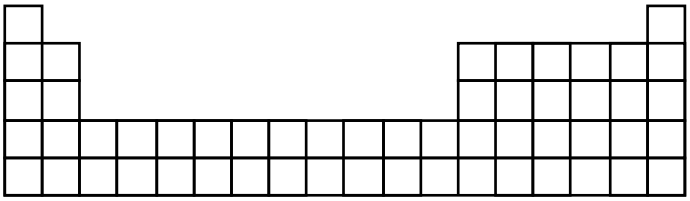
Q 5 What is the electronic configuration of the ground state of the magnesium cation, Mg^{2+} ?

A , $1s^2\ 2s^2\ 2p^6\ 3s^2$
B , $s^2\ 2s^2\ 2p^6\ 3s^1$
C , $1s^2\ 2s^2\ 2p^6$
D , $1s^2\ 2s^2\ 2p^4\ 3s^2$.

Q 6 When ice melts to form liquid water at 0^oC, there is a contraction in volume. This is due to

A , the molecules contracting in size
B , a partial disruption of the hydrogen bonded network of ice on melting
C , the absorption of heat during the melting process
D , the dissolving of air into the water during the melting process.

Q 7 Given the overall lay out of the empty periodic table shown below (up to element 54),



answer the following question.

If X represents an element of atomic number 9 and Y the element of atomic number 20, the compound formed by these elements would be

A , ionic with formula YX_2
B , covalent with formula YX_2
C , ionic with formula YX
D , covalent with formula YX.

Q 8 Manganese ions (Mn^{2+}) can be oxidised by persulfate ions ($S_2O_8^{2-}$) according to the two following half- equations.

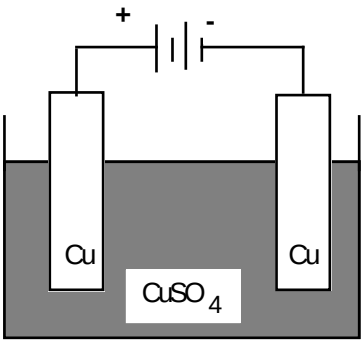
$$S_2O_8^{2-} + 2e^- \longrightarrow 2SO_4^{2-}$$

$$Mn^{2+} + 4H_2O \longrightarrow MnO_4^- + 8H^+ + 5e^-$$

How many moles of $S_2O_8^{2-}$ are required to oxidise 1 mole of Mn^{2+} ?

A , 2.5
B , 2.0
C , i1.0
D , 0.4.

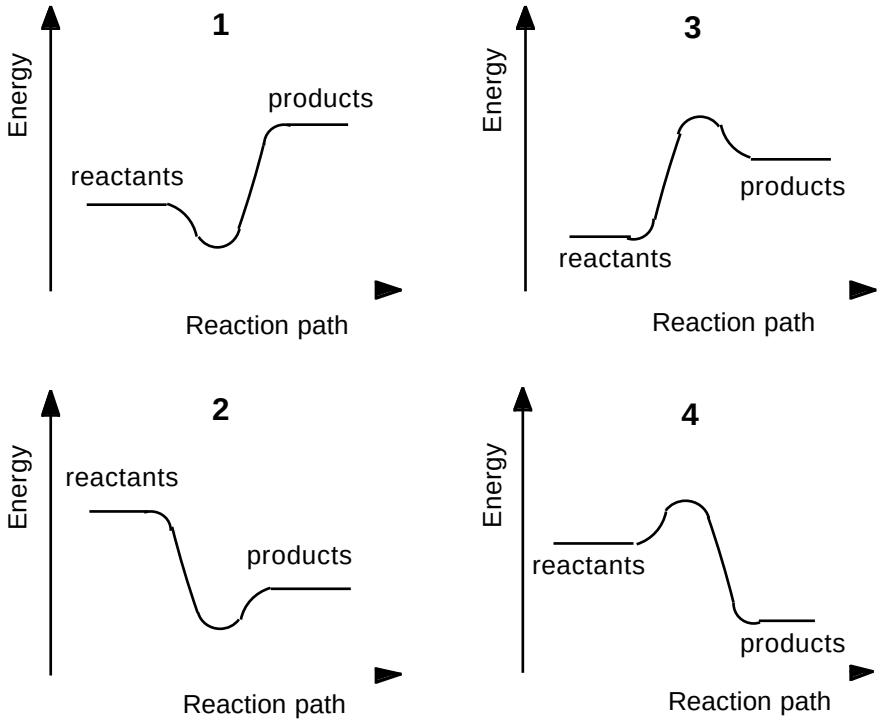
Q 9 The diagram below shows an electrolysis cell which contains 1L of an aqueous 1M copper(II)sulfate solution.



If 0.4 moles of electrons pass through the cell, the concentration of copper ions after passage of the charge will be,

A , 0.4 M
B , 0.8 M
C , 1.0 M
D , 1.2 M.

Q 1 0 The graphs below represent changes in potential energy during the course of a chemical reaction.

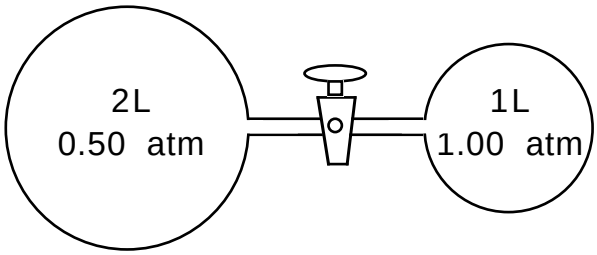


Which one of these graphs would correspond to the reaction represented by the following equation?

$$CH_4\,(g) + O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(g)$$

A , 1
B , 2
C , 3
D , 4.

Q 1 1



Hydrogen gas is contained in two vessels connected by a closed stopcock as shown in the diagram. The volumes and pressures are also shown. When the stopcock is opened and the gases allowed to mix at constant temperature, the final pressure will be (neglecting the volume of the tube between the bulbs)

A , 0.50 atm.
B , 0.75 atm.
C , 0.67 atm.
D , 1.50 atm.

Q12 At $5^{o}C$ the equilibrium constant for self dissociation of water into hydroxyl ions and hydrogen ions is 1.82×10^{-15}. At this temperature pure water has a pH of

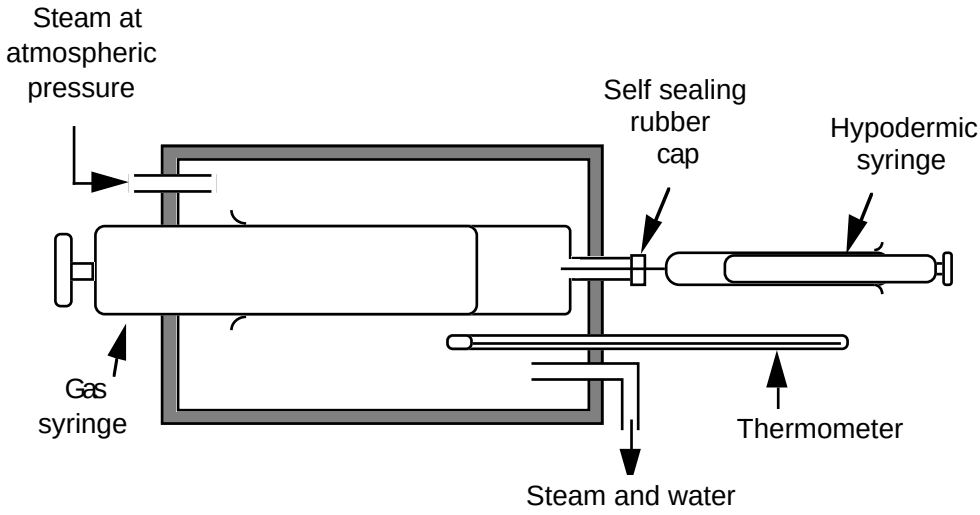
A , 7.00
B , 7.37
C , 7.76
D , 6.63.

Q 1 3 Sulfur dioxide reacts with water to form sulfurous acid (H_2SO_3) and is called the acid anhydride of that acid.

The anhydrides of sulfuric and nitric acids are:

A , SO_3 and NO
B , SO_3 and N_2O_5
C , SO_4^{2-} and NO_2
D , SO_3 and N_2O_3.

Q14



The apparatus shown above can be used to determine the relative molecular mass of a volatile liquid. Firstly the liquid, L, is drawn into a graduated hypodermic syringe from a bottle. L is then introduced into the gas syringe through a self sealing rubber cap and the hypodermic syringe is then removed. The liquid turns into vapour and the volume of vapour produced is recorded. The thermometer reading is also noted. Which of the following liquids could NOT be successfully used in the same way as L in this experiment?

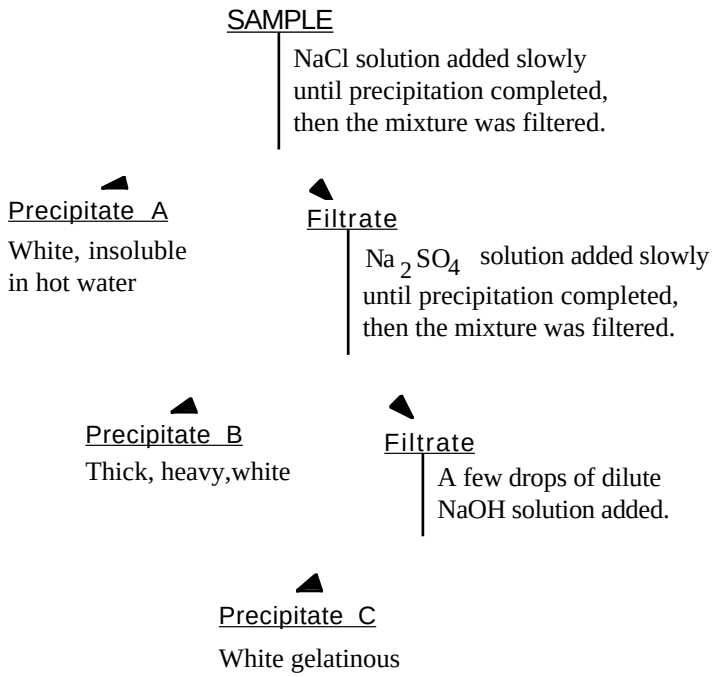
Liquid	Relative molecular mass	Boiling Pt. (^{o}C)	Density (g cm-3)
A	72	79	0.80
B	120	61	1.48
C	154	76	1.59
D	92	110	0.86

Q15 The elements lead, silicon, germanium, tin and carbon all lie in the same group of the periodic table. Which of the following is true?

A , Like carbon, all the elements are non-metals
B , Carbon is closer in properties to silicon than tin is to lead
C , Tin is closer in properties to lead than carbon is to silicon
D , Like tin, all the elements are metals.

SECTION B: Candidates should answer any **three** (3) of the four questions in this section. Be sure that **ALL** relevant working is shown in your answer to numerical questions. You should devote 60 minutes to this section.

Q 1 6 (a) A student was given a sample of a colourless solution containing three cations and was asked to identify the cations. The student carried out a series of reactions as shown in the flow chart below:



(i) From the information above, suggest three cations which could be in the sample and would form the precipitates A, B and C. Give the formula for each precipitate.

(ii) Give an additional test which would help to confirm the presence of each cation.

(iii) Name any other cations that would fit the requirements for precipitates A, B, and C.

(b) A steel sample can be analysed for iron content by dissolving the steel in dilute sulfuric acid to form iron(II) ions.
The acidified solution containing the iron(II) ions is then titrated with potassium dichromate solution from a burette to oxidise the iron(II) ions to iron(III) ions.

(i) Write a balanced ionic equation to show the reaction of iron with the dilute acid.

(ii) Write balanced ionic equations to show separately the oxidation and reduction reactions taking place during the titration. Use these two equations to derive a balanced equation to show the overall reaction taking place during the titration.

(iii) 1.350 g of steel was dissolved in excess dilute sulfuric acid then titrated with 0.20 mol L^{-1} potassium dichromate solution. 18.75 mL of the potassium dichromate solution was needed to reach the end-point.

1) Calculate the number of moles of iron(II) ions in the solution (show working).
2) Calculate the percentage by mass of iron in the steel sample (show working).

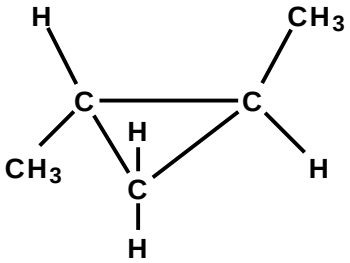
[Relative atomic mass Fe = 55.85]

Q 1 7 Before the days of modern spectroscopic analyses, chemists used to determine the structures of unknown compounds by painstaking experiments, meticulous observation, and careful inference from their results. Care to match wits with one of the "oldies"?

An (g)olden-day chemist had a sample of a carefully purified substance which she named *pleh*. Combustion of 2.20 g of *pleh* in air gave 6.914 g of carbon dioxide and 2.828 g of water. The canny chemist (yes, she was Scottish) noted that *pleh* did not react with bromine in the dark but did react with bromine slowly in sunlight with the formation of acrid vapours. By careful work it was shown that 5.60 g of *pleh* reacted with 12.78 g of bromine to give 11.91 g of *bromopleh* isolated as an oily liquid. The evolved acrid vapours dissolved avidly in water to give a strongly acidic solution that required 320.0 mL of 0.250 M aqueous sodium hydroxide to neutralise it. By very careful distillation of *bromopleh*, our highland chemist was able to separate this oily liquid into three, and only three, different fractions with slightly, but significantly, different boiling points. Aha! That proves it; the compound is clearly *trans*-1,2-dimethylcyclopropane.

Justify this conclusion from the above results! Show all workings and logic.

[Relative Atomic masses: H = 1, C = 12, O = 16, Br = 79.9].



trans - 1,2-dimethylcyclopropane

Q 1 8 The formation of metallic iron, sodium and chromium are examples of different oxidation-reduction processes.

(a) Name the reducing agents which contribute to the production of iron in the blast furnace and write equations for their participation.

(b) The electrowinning of sodium is often accomplished by the Downs Process. Molten sodium chloride is electrolysed between a graphite anode and an iron cathode. Draw a diagram with associated equations to illustrate the essential features of the process and write a sentence or two to explain:

(i) Why the salt has to be molten.

(ii) Why the anode cannot be iron.

(iii) Why aqueous sodium chloride solution cannot be used.

(iv) Why is sodium produced by electrochemical reduction rather than by the use of chemical reducing agents similar to those used in the blast furnace?

(c) In the Thermite Process chromium metal can be produced by igniting a mixture of chromium(III)oxide and aluminium powder. Write an equation for this process and indicate the oxidising and reducing agents involved.

Q 1 9 The dissociation of nitrosyl chloride into nitric oxide and chlorine takes place according to the equation:

$$2NOCl\ (g) \rightleftharpoons 2NO\ (g) + Cl_2\ (g)$$

Varying amounts of the three gases were placed in a container and allowed to come to equilibrium at two different temperatures. The equilibrium concentrations of the three gases obtained are tabulated below:

Temperature	Concentrations in mol L^{-1}		
	NOCl	NO	Cl_2
230 °C	2.33×10^{-3}	1.46×10^{-3}	1.15×10^{-2}
465 °C	3.68×10^{-4}	7.63×10^{-3}	2.14×10^{-4}

(a) Write an expression for the equilibrium constant, K, for this reaction, in terms of the concentrations of NOCl, NO and Cl_2.

(b) Calculate the value of K at each of the temperatures, 230°C and 465°C.

(c) Does the variation of the equilibrium constant with temperature indicate that the reaction is endothermic or exothermic? Explain.

(d) The energy change (ΔH) involved in the above reaction is 38 kJ per mole of nitrosyl chloride decomposed.

Rewrite the equation for the dissociation of one mole of nitrosyl chloride and complete the description of the reaction by specifying ΔH (sign and magnitude) for the reaction you have written.

(e) The reaction is carried out in a sealed vessel, at constant temperature. If the pressure in the vessel were halved by removal of half the contents, and equilibrium were then re-established, at the same temperature, would the concentration of chlorine be halved? Explain your answer.

(f) In another experiment the volume of the reaction vessel was halved, at constant temperature. When equilibrium is re-established what effect would halving the volume have had on the equilibrium constant?