AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1993

General Instructions

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

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

(3) **Use blue or black pen to write your answers**, pencil is not acceptable.

(4) Rough working must be done only in the indicated areas of the answer book.

(5) You are not permitted to refer to books or periodic tables and the only permitted aid is a non-programmable electronic calculator.

(6) You are permitted **15 minutes** to read the paper and supply the requested information on the cover of the answer book, followed by **120 minutes** to work the questions.

(7) Relevant data that may be required for a question will be found on page 2.

DATA

Avogadro constant	6×10^{23} mol^{-1}
1 faraday	96,486 coulombs
1 coulomb	1 amp sec
Universal gas constant (R)	8.314 J K^{-1} mol^{-1} 8.206×10^{-2} L atm K^{-1} mol^{-1}
Standard temperature and pressure (STP)	273 K and 101.3 kPa 0°C and 101.3 kPa 0°C and 1 atm
Molar volume of ideal gas at STP	22.4 L
Density of $CO_{2(s)}$	1.35 g/mL

Heats of formation (ΔH_f°)

Carbon monoxide (CO)	= -111 kJ mol^{-1}
Carbon dioxide (CO_2)	= -393 kJ mol^{-1}
Water (H_2O)	= -242 kJ mol^{-1}
TNT ($C_7H_5N_3O_6$)	= -30 kJ mol^{-1}
Nitroglycerine ($C_3H_5(NO_3)_3$	= -350 kJ mol^{-1}

Relative atomic masses:

Ag	107.87	Al	26.98	Br	79.90
C	12.01	Ca	40.08	Ce	140.12
Cl	35.45	Cr	52.00	Cu	63.55
F	19.00	Fe	55.85	H	1.008
He	4.003	I	126.90	Mg	24.31
Mo	95.94	N	14.01	Na	22.99
Ne	20.18	O	16.00	P	30.97
S	32.06	Si	28.09	Ta	180.95
U	232.03	Zr	91.22		

SECTION A

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

Q1 An isotope of the element polonium, of atomic mass 210, is strongly radioactive and each day one two-hundredth part of it changes into an inactive isotope of lead. Approximately how many atoms of lead are formed in one day from one milligram of ^{210}Po?

A 1.5×10^{16}

B 3×10^{18}

C 1.23×10^{19}

D 3×10^{21}

E 1.2×10^{22}

Q2 Which of the following aqueous solutions contains the same number of solute particles as are contained in 250mL of 2M sodium chloride

1 1 L of M ethanol, C_2H_5OH

2 250 mL of 3M calcium chloride, $CaCl_2$

3 500 mL of M hydrochloric acid, HCl

4 500 mL of M ethanoic acid, CH_3CO_2H

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 3, 4 only correct

E 4 only correct

Q3 In which of the following is there an element with the same oxidation number as that of chromium in $K_2Cr_2O_7$?

1 Cl_2O_7

2 $Fe(CN)_6^{3-}$

3 VO_2^+

4 K_2MnO_4

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 4 only correct

E all are correct

Q4 The successive ionisation energies in kJ/mol of an element **X** are 740, 1500, 7700, 10500, 13600, 18000, 21700. What ion is the most likely to be formed when **X** reacts with chlorine?

A $\mathbf{X}^{2-}$

B $\mathbf{X}^{-}$

C $\mathbf{X}^{+}$

D $\mathbf{X}^{2+}$

E $\mathbf{X}^{3+}$

Q5 Which of the following are acid-base conjugate pairs?

1 HCO_3^- and CO_3^{2-}

2 NH_4^+ and NH_2^-

3 HCl and Cl^-

4 H_3O^+ and OH^-

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 4 only correct

E all are correct

Q6 The standard enthalpies of formation for carbon dioxide and formic acid are -393.7 kJ mol^{-1} and -409.2 kJ mol^{-1} respectively. The enthalpy change, in kJ mol^{-1} for the reaction

$$H_2(g) + CO_2(g) \longrightarrow HCOOH(l)$$

would be

A -802.9

B -414.7

C -15.5

D +15.5

E +802.9

Q7 Which of the following molecules would be expected to be linear?

1 H_2S

2 PH_3

3 H_2O

4 CO_2

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 4 only correct

E all are correct

Q8 Which of the following statements about the elements Mg, Ca, Sr and Ba and their compounds is **not** true?

A The solubility of the hydroxides in water increases with increasing atomic number.

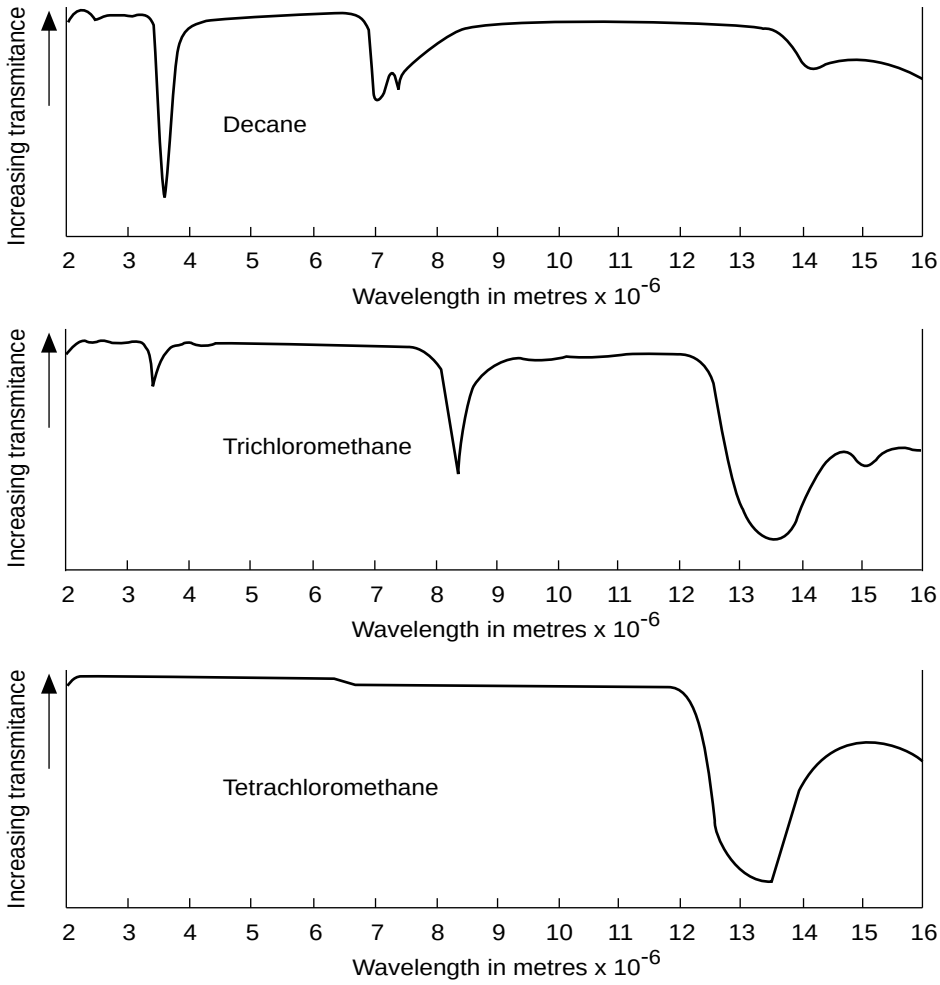
B The pure chlorides are all liquids at room temperature.

C The elements all react with water or steam to give hydrogen.

D The thermal stability of the carbonates increases with increasing atomic number.

E The elements invariably form ions of oxidation number +2.

Q9 The infrared absorption spectra of decane, trichloromethane and tetrachloromethane are shown below.



Reasonable deductions from these spectra include that

1 C—H bonds absorb radiation of wavelength 3.5×10^{-6}

2 C—C bonds absorb radiation of wavelength 7×10^{-6}

3 C—Cl bonds absorb radiation of wavelength 13.5×10^{-6}

4 C—H bonds absorb radiation of wavelength 8.3×10^{-6}

A 1, 2, 3 only correct

B 1, 3 only correct

C 2, 4 only correct

D 4 only correct

E all are correct

Q10 Which of the following statements cocerning the transition elements in the series scandium to zinc is incorrect?

A Most form coloured complex ions

B Most have at least one unpaired electron in a *d*-orbital of a cation

C The most common oxidation state is +1

D All have the ability to form complex ions

E Many exhibit catalytic activity in the elemental form or as one of their simple compounds

Q11 Which of the following formulae can represent more than one compound?

1 CH_4O

2 $C_2H_2Cl_2$

3 H_2CO_2

4 C_2H_6O

A 1, 2, 3 only correct

B 1, 2 only correct

C 2, 4 only correct

D 3 only correct

E 4 only correct

Q12 0.100 moles PCl_5 were introduced into an evacuated 2.0 L flask and heated to 400°C. When the following reaction

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

reached equilibrium analysis showed that 0.060 moles $Cl_{2(g)}$ were present. This data shows that the equilibrium constant for the reaction at 400°C is

A 4.5×10^{-2}

B 3.6×10^{-2}

C 1.8×10^{-3}

D 9.0×10^{-2}

E 0.9×10^{-3}

Q13 The standard electrode potentials of some electrodes are as follows:

I	$Zn^{2+}_{(aq)}\|Zn_{(s)}$	-0.75 V
II	$Cd^{2+}_{(aq)}\|Cd_{(s)}$	-0.40 V
III	$Ni^{2+}_{(aq)}\|Ni_{(s)}$	-0.25 V
IV	$Cu^{2+}_{(aq)}\|Cu_{(s)}$	+0.32 V
V	$Ag^{+}_{(aq)}\|Ag_{(s)}$	-0.76 V

The cell with the smallest potential is made up of the electrodes

A **I** and **II**

B **I** and **III**

C **I** and **V**

D **II** and **III**

E **III** and **IV**

Q14 Consider 1 g of each of the following substances at STP. Which occupies the greatest volume?

A Ethane

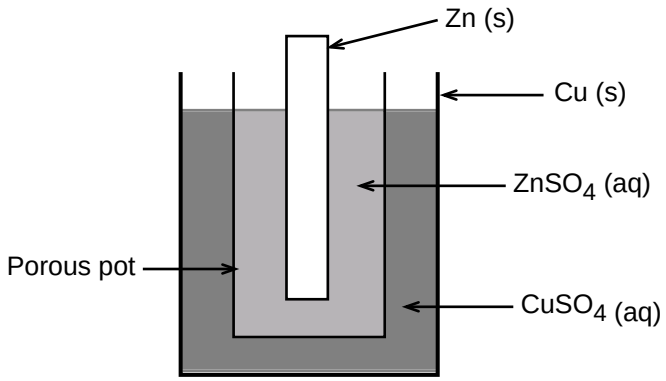
B Fluorine

C Hydrogen sulfide

D Oxygen

E Neon

Q15 The diagram below represents a Daniell cell. When the zinc rod and the copper container are connected as part of a completed electrical circuit, a current flows in this circuit. Which of the following statements about the system is **NOT** correct?



$E^{\circ}_{Zn^{2+}|Zn}$ = -0.76 V

$E^{\circ}_{Cu^{2+}|Cu}$ = +0.34 V

A Copper is deposited around the copper container.

B Electrons flow from the zinc to the copper through the external circuit.

C The zinc electrode gradually dissolves.

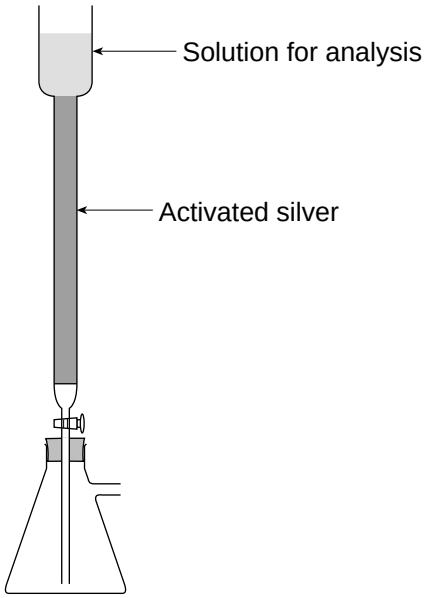
D If both the solutions are molar, then the cell can produce a maximum potential of 1.10 volts.

E Sulfate ions migrate through the porous pot from the zinc compartment to the copper compartment.

SECTION B

Candidates should answer any three (3) of the four questions in this section.
Candidates are advised that the correct use of significant figures will be taken into consideration when marking answers to these problems. Candidates are also advised that steps to the solution of problems must be clearly explained. Marks will be deducted for untidy and poorly explained answers.

Q16 The so called "silver reductor" is a glass column filled with activated silver (see diagram). Solutions of certain ions passed down the column are quantitatively reduced to a lower oxidation state.



One such application of the silver reductor is found in the analysis of copper in brass. Typically a sample of brass is dissolved in nitric acid, diluted with 2 M HCl and passed down the silver reductor. The solution and washings from the column are collected in a solution of Fe^{3+}. The reduced copper is oxidised by the Fe(III) to afford Fe(II) which can in turn be titrated in a redox process using Ce(IV). During this titration the Ce(IV) is itself reduced to Ce(III).

(a) During the dissolution of the brass the Cu is converted to Cu^{2+} and the NO_3^- anion reduced to NO_2.

Write ionic half equations for each of these processes, and hence a balanced ionic equation for the overall process.

(b) The silver reductor reduces Cu^{2+} to Cu^{+}.

Write an ionic half equation for this process and a balanced ionic equation for the subsequent reduction of Fe^{3+} by the Cu^{+}.

(c) (i) Deduce a relationship for mg of Cu in the initial sample with 1 mL of 0.0100 M Ce^{4+}, used as the final titrant.

(ii) Using your answer from the previous question calculate the weight % Cu in a sample of brass, based on the following data.

A sample of brass weighing 1.7062 g was dissolved in concentrated nitric acid and then diluted to a total volume of 250.0 mL, in a volumetric flask, with 2 M HCl. Three 20.0 mL samples of this solution were then run down separate "silver reductors" and the solutions collected in 30.00 mL volumes of 0.5 M ammonium iron(III) sulfate in dilute sulfuric acid. Titration of each of these solutions with 0.1031 M cerium(IV) sulfate solution gave titres of 15.50, 15.45 and 15.53 mL respectively.

(d) Suggest an alternative analytical procedure which might be applicable to this problem.

Q17 (a) (i) The behaviour of gases has occupied a good deal of interest over the years. We describe as "ideal" those gases which obey the ideal gas equation over some range of temperature and pressure.
Write down the ideal gas equation in its commonly encountered form.

(ii) Show that both sides of your ideal gas equation have units of energy.

(b) (i) For a gas that is thermally insulated rearrange the ideal gas equation to the form y = mx + b, with P as the dependant variable.

(ii) What is the independent variable in your equation?

(iii) Table 1 gives data recorded for a given sample of a gas at a constant temperature of 37°C (physiological temperature). With reference to Table 1, does this gas obey the ideal gas equation over the range of P and V for which data are given?

Table 1

Pressure (atmospheres)	Volume (litres)	Pressure (atmospheres)	Volume (litres)
5.09×10^{-3}	1000	0.0153	332
6.705×10^{-3}	752	0.0204	250
7.63×10^{-3}	668	0.0509	100
0.0102	498	0.102	50

(iv) Determine the average experimental molecular mass of the gas sample, given that 8.69 grams of gas were used in the experiment.

(c) (i) Deviations in ideal behaviour are noted for many gases. Inset A of Fig 1 demonstrates the P versus V behaviour of one such deviation. Explain what deviation from ideal behaviour has occurred.

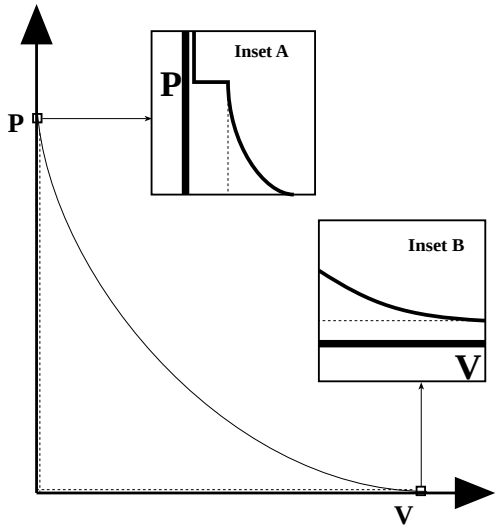


Figure 1: P versus V of a gas

(ii) Given that the gas studied was carbon dioxide use your knowledge of the molecular structure of carbon dioxide to suggest why there is a deviation from the ideal gas law and why there is such a volume change.

(iii) The pressure at which the deviation from ideal behaviour first occurs in inset A is known as the critical pressure (P_{crit}) and has a value of 72.9 atmospheres at room temperature for CO_2. Give the name of the process that occurs at P_{crit} for CO_2 and estimate the magnitude of the energy associated with this change.

(d) In inset B of Fig 1, it is noted that as the volume of the gas system approaches very large values, the system does not approach zero on the P axis, but some fixed (finite) value. Incorporate this feature of behaviour of an ideal gas by addition of a term into your equation of state for a gas.

Q18 Prior to the advent of modern spectroscopic methods for determining molecular structure the organic chemist relied heavily upon chemical tests to identify building blocks within molecules. Some of these tests are well known

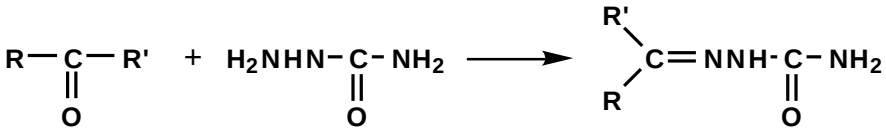
eg. $Cr(VI) \rightarrow Cr(III)$ used to help identify primary and secondary alcohols.

$Mn(VII) \rightarrow Mn(II)$ used under controlled conditions to help identify carbon-carbon multiple bonds.

Less well known are the mild oxidants such as the so called Tollens reagent

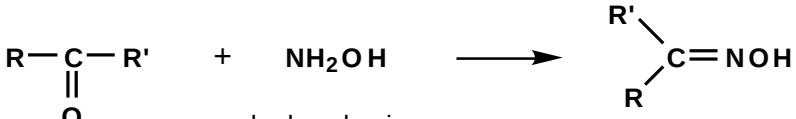
$Ag^+ \rightarrow Ag(s)$

which is useful for distinguishing ketones from aldehydes. Finally we can add a set of reactions



semicarbazide

R and R' represent alkyl groups



hydroxylamine

which were frequently used to form crystalline derivatives from aldehydes and ketones.

Try now to match your skills with the classical organic chemist and solve the following problem.

*Oil of lemon grass contains a substance **A** which analyses C 78.89%, H 10.59%. **A** reacts with both Tollens reagent and hydroxylamine. Oxidation of **A** affords a new compound **B** which is soluble in both sodium hydroxide and sodium bicarbonate.*

(a) Suggest an empirical formula for **A** based on this analytical data.

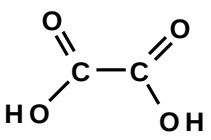
(b) Suggest which functional groups might be present in **A** and **B**.

*Reduction of **A** by the addition of hydrogen in the presence of palladium affords **C**, and further reduction of **C** with sodium borohydride affords **D**, which has a relative molecular mass (molecular weight) of 158 to the nearest whole number. **D** does not decolourise cold potassium permanganate but does react with aqueous chromium (VI) to ultimately afford **E**.*

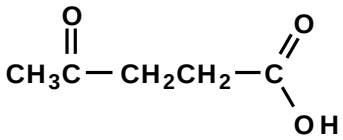
(c) What functional group is likely to be in **D**.

(d) How many double bonds are likely to be in **A**.

(e) Careful reaction of **A** with ozone followed by oxidation affords three products in equimolar amounts. these were propanone (acetone), oxalic acid (**F**) and (**G**).



(**F**)

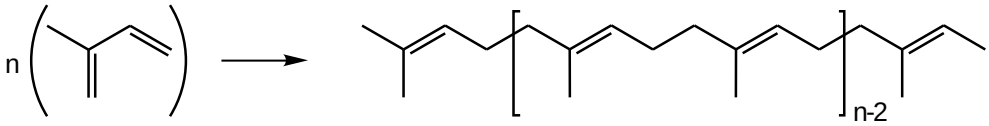


(**G**)

What structures might you suggest for **A** based on this data?

The so called ispoprene rule states "terpenes can be considered to arise from the head to tail link of isoprene units"

ie

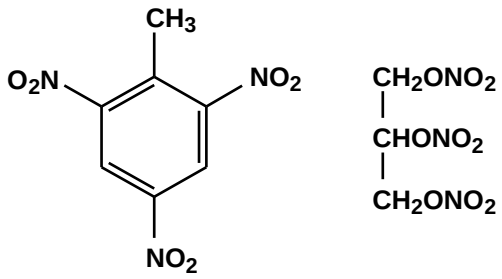


(f) Given that **A** is a regular terpene which obeys the isoprene rule which of your structures in (e) can you now eliminate based on this rule.

(g) In practice **A** is known to be a mixture of two *cis/trans* (geometrical isomers), give structures for each of these compounds.

(h) Identify compounds **B**, **C**, **D** and **E**.

Q19 (a) Trinitrotoluene (TNT), **1**, and nitroglycerine, **2**, are two of the most commonly used



1 **2**

compounds in the production of high explosives. When ignited they decompose very rapidly and exothermically. For example, TNT, a solid at normal temperatures, decomposes as follows:

$$2C_7H_5N_3O_6(s) \longrightarrow 12CO(g) + 5H_2(g) + 3N_2(g) + 2C(s) + \text{energy}$$

(i) Write a balanced equation for the reaction that occurs when nitroglycerine(l) explodes given that the only products are $N_2(g)$, $CO_2(g)$, $O_2(g)$ and $H_2O(g)$.

(ii) Calculate the $\Delta H^{\circ}_{(reaction)}$ for the decomposition of nitroglycerine(l).

(iii) Calculate the $\Delta H^{\circ}_{(reaction)}$ for the decomposition of TNT(s).

(iv) What makes compounds **1** and **2** suitable for use in the manufacture of high explosives. Give **four** reasons. [Hint : The required information can be abstracted from the two equations.]

(b) Compound **A** is a white crystalline ionic solid which, like **1** and **2**, is extensively used as an 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 as a by-product. **D** is used commercially as a general anaesthetic and as a compressed gas propellant in whipped cream. The action of dilute nitric acid on copper produces **E** and H_2O. **E** is a colourless, paramagnetic gas that is produced commercially by means of the catalytic oxidation of NH_3. At high pressures and moderate temperatures **E** rapidly disproportionates to **D** and a brown gas **F**. In the presence of **C**, **E** is also converted to **F**. When dissolved in water **F** forms HNO_3 and **E**.

Identify compounds **A - F** and write balanced equations for each of the reactions mentioned above.