

AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1992

General Instructions

- (1) This paper is in **two** sections and you must answer each section according to the instructions.
ie. Section A: Answer **ALL** questions
Section B: Question 16 is **compulsory**
Answer **any two** of Questions 17, 18 or 19
- (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	$6 \times 10^{23} \text{ mol}^{-1}$					
1 faraday	96,486 coulombs					
1 coulomb	1 amp sec					
Universal gas constant (R)	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$					
	$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$					
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					
Ionic molar conductivities	$\lambda_{\text{H}^+} = 35.0 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$					
	$\lambda_{\text{HCO}_3^-} = 4.45 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}$					
Dissociation constants for carbonic acid	$\text{pK}_{\text{a}1} = 6.35$					
	$\text{pK}_{\text{a}2} = 10.33$					
Relative atomic masses:	Ag	107.87	Al	26.98	Br	79.90
	C	12.01	Ca	40.08	Cl	35.45
	Cr	52.00	Cu	63.55	F	19.00
	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 In the nineteenth century, there was considerable doubt over the formula of zirconium oxide. The relative atomic mass of zirconium (Zr) was thought to be about 90. The relative molecular mass of the volatile chloride was found to be 236 (Cl = 35.5). This evidence suggests that the most likely formula for the oxide of zirconium is

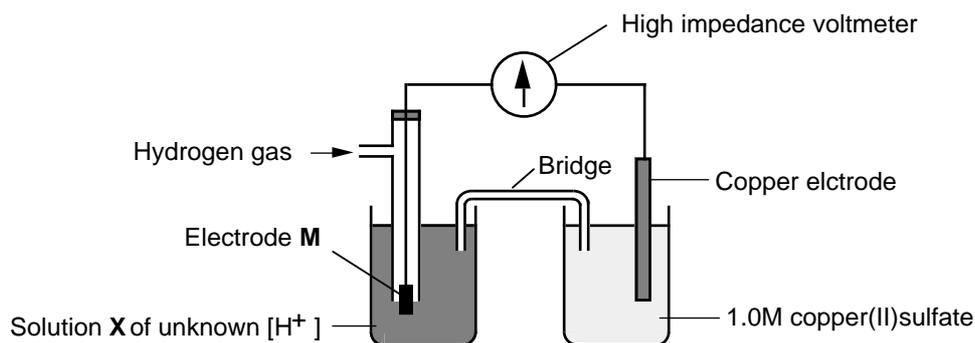
- A ZrO
- B ZrO₂
- C ZrO₃
- D Zr₂O₃
- E Zr₂O₅

Q2 What is the particle **X** in the following nuclear reaction?



- A ${}_{11}^{24}\text{Na}$
- B ${}_{10}^{24}\text{Ne}$
- C ${}_{12}^{24}\text{Mg}$
- D ${}_{14}^{24}\text{Si}$
- E ${}_{11}^{23}\text{Na}$

Q3 A student set up the following apparatus to determine the hydrogen ion concentration of solution **X**.



The cell is: $\text{M} [\text{H}_2(\text{g})] | 2\text{H}^+(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}(\text{s})$

The potential for the cell was found to be +0.43 volts. From tables the potential for the copper electrode was found to be +0.34 volts.

The potential of the hydrogen electrode was

- A +0.76 V
- B +0.09 V
- C zero (since the hydrogen electrode is the standard)
- D -0.09 V
- E -0.76 V

- Q4** The ground-state electronic configurations of five elements are shown below. For which element would you expect the value of the first ionisation energy to be the greatest?

	1s	2s	2p
A	↑		
B	↑↓		
C	↑↓	↑	
D	↑↓	↑↓	
E	↑↓	↑↓	↑

- Q5** Which change would have a negative ΔH value?

- A** $\text{Na(s)} \longrightarrow \text{Na(g)}$
B $\text{Na(g)} \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$
C $\text{Na}^+\text{Cl}^-(\text{s}) \longrightarrow \text{Na}^+(\text{g}) + \text{Cl}^-(\text{g})$
D $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g})$
E $\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$

- Q6** The data below refer to eight elements, lettered **M** to **T** (these letters are **NOT** chemical symbols).

Element	M	N	O	P	Q	R	S	T
Atomic number	Z	$Z + 1$	$Z + 2$	$Z + 3$	$Z + 4$	$Z + 5$	$Z + 6$	$Z + 7$
Molar enthalpy of vaporisation (kJmol^{-1})	2.8	3.4	3.3	1.8	89	129	294	377
Boiling point (K)	73	93	83	23	1163	1373	2673	2973

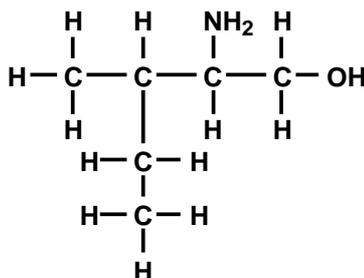
From these data, it can be deduced that

- A** **T** is in the same group of the periodic table as helium
B the elements are all in the same period of the periodic table
C **N** is a metallic element
D **S** could be described as a giant structure or a molecular network
E **M** is a group 1 element in the periodic table
- Q7** The solubility product of silver chromate is $1 \times 10^{-12} \text{ mol}^3\text{L}^{-9}$. In a solution in which $[\text{CrO}_4^{2-}]$ is $1 \times 10^{-4} \text{ molL}^{-3}$, the maximum $[\text{Ag}^+]$, in molL^{-3} , is
- A** 0.5×10^{-8}
B 1×10^{-8}
C 1×10^{-6}
D 0.5×10^{-4}
E 1×10^{-4}

Q8 When aqueous sodium hydroxide is added to an aqueous solution of chromium(III) ions, a green-blue precipitate is first formed which re-dissolves to give a green solution. This green colour could be due to

- A $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- B $[\text{CrO}_4]^{2-}$
- C $[\text{Cr}(\text{OH})_4]^-$
- D $[\text{Cr}(\text{OH})_3(\text{H}_3\text{O})_3]$
- E $[\text{Cr}_2\text{O}_7]^{2-}$

Q9 The compound



is called

- A 2-ethyl-3-aminobutan-4-ol
 - B 3-amino-2-ethylbutan-4-ol
 - C 3-methyl-4-aminopentan-5-ol
 - D 4-amino-3-methylpentan-1-ol
 - E 2-amino-3-methylpentan-1-ol
- Q10** The experimentally determined melting point of a compound is lower than expected. If each of the following procedures is applied to separate samples of the prepared compound, which is likely to **NOT** change the melting point?

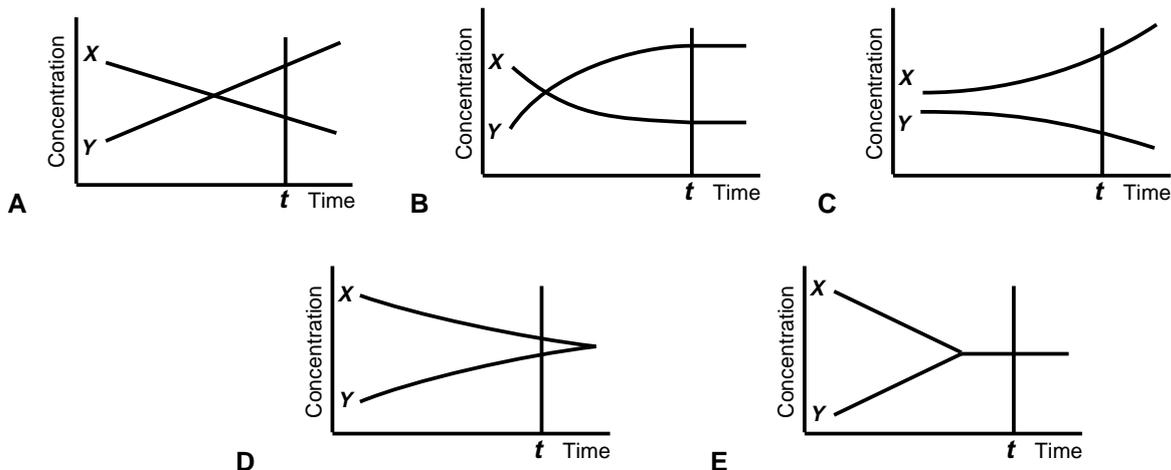
- A Drying to remove solvent
- B Mixing with pure compound
- C Grinding to a finer powder
- D Recrystallising from a solvent
- E Adsorbing impurities on charcoal

Q11 The species $\text{Mo}(\text{CN})_8^{4-}$, TaF_8^{3-} and $\text{U}(\text{NCS})_8^{4-}$ all contain metal ions with a coordination number of eight (8) even though their geometries are different. Various sets of hybrid orbitals have been proposed to account for the bonding in one or other of these complex ions. Of the sets of hybrids listed below which **cannot** be considered in discussing the bonding in one or more of the species above.

- 1 d^4sp^3
- 2 d^5sp
- 3 d^4sp^2
- 4 d^5p^3
- 5 d^3fsp^3

- A 2 and 3
- B 4 alone
- C 4 and 5
- D 1 and 4
- E 5 alone

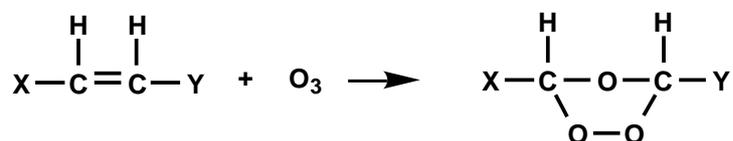
Q12 Which diagram could represent the variation in the concentration of X and Y with time in the reversible reaction $X \rightleftharpoons Y$ which comes to equilibrium after time t .



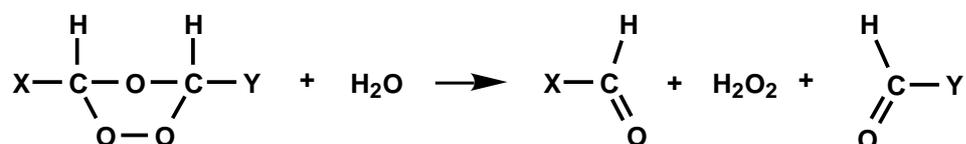
Q13 The electron configuration of atoms of a certain element is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$. The maximum oxidation number of the element is

- A +2
- B +3
- C +4
- D +5
- E +6

Q14 Ozone is a form of oxygen in which the molecules are triatomic. Ozone reacts with compounds containing carbon to carbon double bonds thus:



The product of this reaction can be carefully hydrolysed as shown:

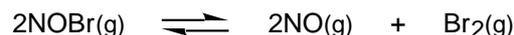


Which of the following would be reasonable uses of either or both of these reactions?

- 1 To find out if a compound contains a carbonyl group.
- 2 To find the percentage of ozone in a sample of partially ozonised oxygen.
- 3 To promote polymerisation of compounds containing double bonds.
- 4 Determining the location of double bonds in suitable compounds.

- A 1, 2, 3 only correct
- B 1, 3 only correct
- C 2, 4 only correct
- D 4 only correct
- E 1, 2, 3, 4 are all correct

Q15 Consider the following reaction (assume an **IDEAL** gas mixture)



A 1.0 L vessel was initially filled with pure NOBr, at a pressure of 4.0 atm, at 300 K. After equilibrium was established, the partial pressure of NOBr was 2.5 atm. What is K_p for the reaction?

- A 0.27
- B 0.45
- C 0.18
- D 0.75
- E none of these

SECTION B

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.

Question 16 is compulsory. You have a choice of answering any two questions of the remaining three questions.

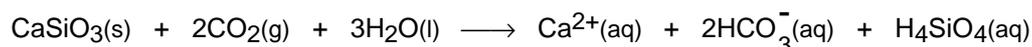
Compulsory question

Q16 (a) Diatoms, microscopic organisms that can be considered to be carbohydrate, are an abundant food source in oceans producing carbohydrates from carbon dioxide and water by photosynthesis.



During their first five years of life blue whales gain 75.0 kg of mass per day by feeding on krill. The blue whale must consume ten times this mass of krill each day. The krill must consume 10.0 kg of diatoms to produce 1.0 kg of krill. Assuming that the mass gain in the first five years of a blue whale's life is due to the consumption of carbohydrates ($\text{C}_6\text{H}_{12}\text{O}_6$), calculate the volume of CO_2 at STP that must be used by the diatoms to produce the carbohydrates consumed by a blue whale in its first five years of life.

- (b) (i) There is 0.23mL of dissolved CO_2 per L of sea water (at 24°C and 1.0 atm). If diatoms can completely remove carbon dioxide from the water they process, what volume of water would they process to produce the carbohydrates required by a blue whale during the first five years of life?
- (ii) What fraction of the total volume of the oceans will be needed to supply the carbon dioxide for the first five years of growth of 1000 blue whales? The volume of the oceans is $1.37 \times 10^{18} \text{ m}^3$.
- (c) Consider the mass of an adult blue whale to be $9.1 \times 10^4 \text{ kg}$. Three percent of the mass of an adult blue whale is nitrogen, when such a blue whale dies, what is the maximum mass of NH_4^+ that can become available to marine organisms?
- (d) Eighteen percent of an adult blue whale's mass is carbon. Carbon can be returned to the atmosphere as carbon dioxide, and then removed from the atmosphere by weathering of rocks containing calcium silicate.



What are the maximum number of grams of CaSiO_3 that can be weathered by the carbon dioxide produced from the decomposition of 1000 adult blue whales, the number estimated to die annually?

Answer any two of the remaining three questions.

- Q17** (a) The arrangement of valence electrons in atoms in molecules can be represented using Lewis structures. Lewis structures of molecules are constructed by using the following rules:
- (1) Sum the valence electrons from **all** the atoms.
 - (2) Use a pair of electrons to form a bond between each pair of bound atoms.
 - (3) Arrange the remaining electrons such that each atom achieves a **noble gas configuration** of valence electrons as, in general, the most stable compounds are those in which the atoms have such a configuration.
 - (4) Third row elements in molecules sometimes exceed the **octet rule**. When it is necessary to exceed the octet rule the extra electrons are placed on the central atom.

Before proceeding further you should be aware that **additional information** is available at the end of the problem if required.

Write Lewis structures for each of the following species:

- CH₄
- NH₃
- SF₆
- CO₂
- SO₃ (This molecule has more than one valid Lewis structure.)

- (b) The **valence shell electron pair repulsion (VSEPR) model** is used by chemists to predict the shapes of molecules. The underlying idea is that the electron pairs surrounding an atom in a molecule arrange themselves so as to **minimise** electron pair repulsions. Consider the following table:-

Molecule	Effective* electron pairs around central atom	Electron Pair Geometry**	Molecular** Structure	Bond Angle
CO ₂	2	linear	linear	180°
SO ₃	3	trigonal planar	trigonal planar	120°
CH ₄	4	tetrahedral	tetrahedral	109.5°
NH ₃	4	tetrahedral	trigonal pyramidal	107°
H ₂ O	4	tetrahedral	angular	104.5°
PCl ₅	5	trigonal bipyramidal	trigonal bipyramidal	see below***
SF ₆	6	octahedral	octahedral	90°

* Multiple bonds count as **one** effective pair of electrons.

** The electron pair geometry refers to the arrangement of the electron pairs about a central atom, whereas the molecular structure refers to the arrangement of atoms in the molecules.

Write the Lewis structure and describe the electron pair geometry and molecular structure for each of the following species:

- CCl₄
 - SCl₂
 - ICl₄⁻
- (c) From the above table it is clear that CH₄, NH₃ and H₂O all have a tetrahedral electron pair geometry, however, the bond angle decreases from left to right. This is because lone pairs of electrons are considered to occupy more space than bonding pairs of electrons. Electron pair interactions decrease in the following manner:

lone pair - lone pair > lone pair - bonding pair > bonding pair - bonding pair.

With this in mind, predict the molecular structures of the following species:

- (i) Br_3^-
 - (ii) BrF_3
 - (iii) SF_4
- (d) The bond angle in SO_3 and SO_2 is 120° . Can you offer a suggestion as to why the bond angle in O_3 and NO_2^- is less than 120° .

Additional information: C is in Group IV, N and P are in Group V, O and S are in Group VI, and the halogens are in Group VII of the Periodic Table.

- Q18** (a) Standard solutions of sodium thiosulphate are employed in volumetric determination of iodine. Unfortunately crystalline sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) is not a satisfactory primary standard and the analyst must first standardise solutions of thiosulfate before using them. One way of achieving this is to stoichiometrically liberate iodine by oxidising iodide ion in acidic solution with bromate ion (BrO_3^-). The iodine liberated can then be used to determine the exact strength of the thiosulfate solution.
- (i) Write half equations for the reduction of bromate to bromide and the oxidation of iodide to iodine.
 - (ii) Using your answer to part (i) construct a balanced ionic equation of the reaction of bromate with iodide in acidic solution.
 - (iii) Given that iodine converts thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$) to the $\text{S}_4\text{O}_6^{2-}$ ion and is itself reduced to iodide. Write a balanced equation for the reaction of sodium thiosulfate with iodine.
 - (iv) In standardising a solution of sodium thiosulfate a chemist found that on average 19.52 mL of solution was required to react with the iodine liberated from 0.05568g of potassium bromate and excess potassium iodide in acidic solution. What was the molarity of the sodium thiosulfate solution?
 - (v) Which indicator might the chemist have used to detect the end point of the titration?
- (b) Carbon monoxide is a toxic gas produced by the incomplete combustion of hydrocarbons, and the estimation of carbon monoxide concentration in flue gases and exhausts is of considerable environmental interest. One way of determining carbon monoxide concentration is to react the gas with iodine pentoxide (I_2O_5), a process which stoichiometrically oxidises the CO and reduces the I_2O_5 to elemental iodine. The latter can be trapped and estimated by titration with standard sodium thiosulfate solution.
- In one such estimation 1.092L (at STP) of a gas mixture was reacted with I_2O_5 . Subsequent titration of the iodine with standard sodium thiosulfate showed that 17.92 mL was required to reach an end point. The standard solution used was prepared by taking 10 mL of the solution prepared in part (a) of this question and diluted to a total volume of 1L in a volumetric flask.
- (i) What was the percentage by volume of CO in the gas sample?
 - (ii) What was the concentration of CO in ppm (to the nearest whole number) in the gas sample?
 - (iii) What sort of compound present in the gas sample might cause this result to be in error.

Q19

It might come as a bit of a surprise but the pH of distilled water is not really 7 (neutral), but is actually about 5.6 (acidic). Upon standing, left open to the air, gases readily dissolve back into freshly distilled water. The amount of gas that dissolves can be shown to be *directly proportional* to the partial pressure of that particular gas above the solution, this is Henry's law. The most common gas that can change the pH of water is carbon dioxide. Once dissolved the carbon dioxide reacts to a tiny degree to form an equilibrium with carbonic acid, a diprotic acid. The carbonic acid is a weak acid and dissociates into ionic products.

- (a) Write down the equilibrium equations and develop expressions for the dissociation constants (k_{a1} and k_{a2}) for carbonic acid.
- (b) Assuming that the final dissociation to yield the carbonate anion can be ignored, write an expression for the pH dependency of the solution in terms of the concentration of carbonic acid.
- (c) Electricity conducts quite well through ionic solutions. How well depends upon the concentration, the valency and the identity of the dissolved ions. For example, a 10^{-2}M KCl solution conducts slightly better than a 10^{-2}M NaCl solution, the difference arising from the difference in the size of the two cations. At low concentrations, say less than 10^{-4}M , it can be said that the total solution conductivity (Λ) is the sum of the products of the molar conductivities of the individual ionic species (λ) by their concentrations.

$$\Lambda = \lambda_{\text{cation}} [\text{cation}] + \lambda_{\text{anion}} [\text{anion}]$$

It should be noted that the electrical resistance of a solution is *inversely* proportional to the solutions conductivity.

Knowing all this an environmental chemist decided that she would try and determine the concentration of atmospheric carbon dioxide, also knowing that CO_2 is the only atmospheric gas that gives an appreciable concentration of ions in aqueous solution. By bubbling air through a conductance cell, she was able to measure the resistance of the solution, (which was readily saturated with CO_2). Given that the partial pressure of CO_2 in air is about 300Pa and that she can measure resistances to within 0.1%, what is the smallest change in CO_2 that she can determine?.