AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1994

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	6.02×10^{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

Relative atomic masses:

Ag	107.9	Al	26.98	B	10.81
Br	79.90	C	12.01	Ca	40.08
Cl	35.45	Co	59.93	Cr	52.00
Cu	63.55	F	19.00	Fe	55.85
Ge	72.59	H	1.008	He	4.003
Mg	24.31	N	14.01	Na	22.99
O	16.00	P	30.97	Rh	102.9
S	32.06	Si	28.09	Ti	47.88
U	238.0	Xe	131.3	Zn	65.38

Atomic numbers:

Al	13	Be	4	Co	27
He	2	N	7	P	15

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 When 4.50 g of Fe_2O_3 is reduced with excess H_2 in a furnace, 2.60 g of metallic iron is recovered. What is the percent yield?

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$

A 31.5

B 57.8

C 70.0

D 82.6

Q2 A sample of a compound of xenon and fluorine contains molecules of a single type XeF_n, where n is a whole number. If 9.03×10^{20} of these XeF_n, molecules have a mass of 0.311 g, what is the value of n?

A 6

B 4

C 3

D 2

Q3 Which is true about equal volumes of CH_4 and O_2 at 20 °C and 1 atm pressure?

A The CH_4 sample has a mass that is one-half that of the O_2 sample.

B The number of O_2 molecules is twice as large as the number of CH_4 molecules.

C The average kinetic energy of the O_2 molecules is one-half that of the CH_4 molecules.

D The average velocity of the O_2 molecules is one-half that of the CH_4 molecules.

Q4 Carbon monoxide gas reacts with hydrogen gas at elevated temperatures to form methanol according to this equation.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

When 0.40 mol of CO and 0.30 mol of H_2 are allowed to reach equilibrium in a 1.0 L container, 0.060 mol of CH_3OH are formed. What is the value of the concentration equilibrium constant K_c?

A 0.50

B 0.98

C 1.7

D 5.4

Q5 Which hydroxides are expected to be amphoteric in aqueous solution?

I $Al(OH)_3$

II $Ca(OH)_2$

III NaOH

IV $Zn(OH)_2$

A I only

B III only

C I and IV only

D I, II and IV only

Q6 Which equation represents an acid-base reaction according to the Lewis definition but not according to the Brönsted-Lowry definition?

A $NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

B $HF(aq) + OH^-(aq) \longrightarrow H_2O(l) + F^-(aq)$

C $Al(H_2O)_6^{3+}(aq) \longrightarrow Al(H_2O)_5(OH)^{2+}(aq) + H^+(aq)$

D $Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow Cu(NH_3)_4^{2+}(aq)$

Q7 Which statement is true about a voltaic cell constructed using the half-cells below? Assume 1 M concentration.

Standard Reduction Potentials: $Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$ -0.74 V

$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$ -0.28 V

A Electron flow in the external circuit will be from chromium to cobalt.

B Chromium will be the cathode.

C As the reaction proceeds, the cobalt will undergo oxidation.

D In the salt bridge connecting the half cells, anions will move towards the cobalt.

Q8 How many minutes will be required to deposit 1.00 g of chromium metal from an aqueous CrO_3 solution using a current of 6.00 amperes?

A 186

B 30.9

C 15.4

D 5.15

Q9 According to valence bond theory, what hybrid orbitals are used by the central atom in SF_4?

A sp^3

B dsp^2

C dsp^3

D d^2sp^3

Q10 Given these values of $\Delta H°$:

$CS_2(l) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$ $\Delta H° = -1077$ kJ

$H_2(g) + O_2(g) \longrightarrow H_2O_2(l)$ $\Delta H° = -188$ kJ

$H_2(g) + 1/2\ O_2(g) \longrightarrow H_2O(l)$ $\Delta H° = -286$ kJ

What is the value of $\Delta H°$ for this reaction?

$CS_2(l) + 6H_2O_2(l) \longrightarrow CO_2(g) + 6H_2O(l) + 2SO_2(g)$

A -1175 kJ

B -1551 kJ

C -1665 kJ

D -3921 kJ

Q11 A catalyst increases the rate of a reaction by

A changing the mechanism of the reaction.

B increasing the activation energy of the reaction.

C increasing the concentration of one or more of the products.

D decreasing the difference in relative energy of the reactants and products.

Q12 How many electrons are required to balance the half reaction in which dichromate ion, $Cr_2O_7^{2-}$ is converted to chromium(III) ions in acid solution?

A one

B five

C six

D eight

Q13 What type of radiation is emitted during a nuclear process in which a nucleus with a greater atomic number is formed?

A alpha particles

B beta particles

C positrons

D gamma rays

Q14 The first three ionisation energies of an element X are 735, 1445 and 7730 kJ/mol. The most likely formula for a stable ion of X is

A X^+

B X^{2+}

C X^{3+}

D X^-

Q15 Which substance has the highest melting point?

A silicon carbide, SiC

B phosphorus pentachloride, PCl_5

C sulfur, S_8

D phosgene, $COCl_2$

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) Nitrogen in agricultural materials is often determined by the Kjeldahl method. The method involves a treatment of the sample with hot concentrated sulfuric acid, to convert organically bound nitrogen to ammonium ion. Concentrated sodium hydroxide is then added, and the ammonia formed is distilled into hydrochloric acid of known volume and concentration. The excess hydrochloric acid is then back-titrated with a standard solution of sodium hydroxide, to determine nitrogen in the sample.

0.2515 g of a grain sample was treated with sulfuric acid. Sodium hydroxide was then added and the ammonia distilled into 50.00 mL of 0.1010 M hydrochloric acid. The excess acid was back-titrated with 19.30 mL of 0.1050 M sodium hydroxide. Calculate the following

(i) The number of moles of HCl in 50.0 mL of 0.1010 M hydrochloric acid.

(ii) The number of moles of HCl remaining after the absorption of ammonia.

(iii) The number of moles of HCl consumed by the ammonia and hence the number of moles of ammonia liberated from the grain sample.

(iv) The volume of ammonia (at STP) that would have been derived from the grain sample.

(v) The % of nitrogen in the grain sample.

(vi) The pH of the initial solution of 0.1010 M HCl once the NH_3 was absorbed.

(vii) The pH of the solution at the point in the titration when 19.30 mL of NaOH had been added. Given that K_a for NH_4^+ is 5.7×10^{-10}.

(b) A chemist is confronted with four black powders in unlabelled bottles. They are CuO, FeS, Fe and Ag. She has at her disposal a limited number of reagents, distilled water, 2 M HCl, NaOH, NH_3 and $CuSO_4$ solutions in water. Imagine that you are the chemist and that you may choose one and **only one** of the reagents to identify all four of the powders.

(i) Which reagent would you choose.

(ii) Write balanced equations for the reactions which take place between the four powders and the reagent.

(iii) Write the observations you would expect to make for each reaction.

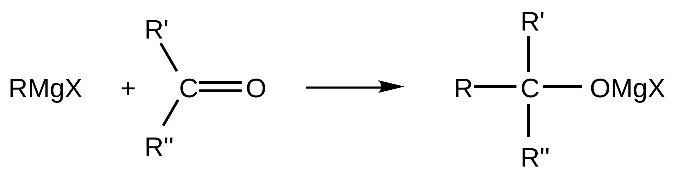
Q17

(a) Grignard compounds are prepared by reaction between organic halogen compounds and magnesium in diethyl ether according to the chemical equation (R represents an alkyl group, X a halogen atom)

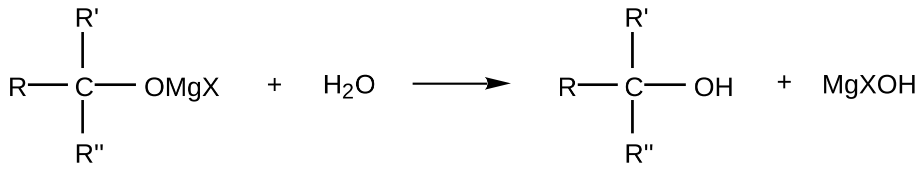
$$RX + Mg \longrightarrow RMgX$$

Write the chemical equation for the preparation of ethyl magnesium bromide.

(b) Grignard compounds react with carbonyl compounds according to the following chemical equation (R' and R" represent a hydrogen atom or an alkyl group)



Hydrolysis of the Grignard compound with water gives an alcohol according to the equation



Which carbonyl compounds give with ethyl magnesium bromide the following final products? Write chemical equations for the reaction between the Grignard compound and the carbonyl compound in question. Use structural formulae.

(i) 1-propanol

(ii) 2-butanol

(iii) 2-methyl-2-butanol

(c) If a Grignard compound is allowed to react with carbon dioxide and the product formed is then hydrolysed with water the final product is a carboxylic acid.

Write the chemical equation for the reaction between carbon dioxide and the Grignard compound which can be prepared from 2-bromopropane. Write also the equation for the subsequent hydrolysis. Use structural formulae.

Q18

Six elements designated for convenience **A**, **B**, **C**, **D**, **E** and **F** (note these symbols bear no relationship to the IUPAC symbols normally used to represent the elements) have the following properties.

- **A**, **E** and **F** have the same number of valence electrons.
- **E** has an energy sub-level which contains 5 electrons, all of which are unpaired, and forms highly coloured compounds.
- The outermost occupied energy levels of **C**, **D** and **F** have the same principle quantum number.
- **B** is the most reactive member of its group, all of which are non-metals.
- The ions of **F** and **B** are isoelectronic.
- **A** combines with **F** to give **FA**, an ionic solid.
- **A** combines with **B** to give **AB**, a gas at room temperature.
- **A** combines with **C** to give $\mathbf{CA_3}$, a poisonous gas.
- **F** and **D** form the compound $\mathbf{F_2D}$, which conducts electricity in the molten state, but not in the solid state.
- **D** as a lower ionisation energy than **C**.
- **D** has a smaller atomic radius than **C**.
- **E** has the smallest atomic radius of its group.
- In its elemental form the molecular mass of **A** is 2.

(a) From the above information place the letters **A**, **B**, **C**, **D**, **E** and **F** on the blank periodic table in your answer book in the positions of the elements they represent.

(b) Provide the name and IUPAC symbols for the six elements relating these to the symbols used in this problem.

Q19

According to the Aufbau principle the orbitals of an atom are filled in the following sequence:

$1s\ 2s\ 2p\ 3s\ 3p\ 4s\ 3d\ 4p\ 5s\ 4d\ 5p\ 6s$

The integer values 1 - 6 in the above sequence refer to the principal quantum number **n** and is related to the size and energy of the orbital. The larger the value of **n** the larger the size and the greater the energy of the orbital. Three quantum numbers are required to describe an orbital: **n**, **l** and $\mathbf{m_l}$**.** The angular momentum quantum number **l** can have integer values 0 to **n**-1 and is related to the shape of an orbital with **l** = 0, 1 or 2 for an *s*, *p* or *d* orbital, respectively. The magnetic quantum number $\mathbf{m_l}$ can have integer values **-l** to **l** including 0 and is related to the number of each type of orbital. For example, if **n** = 1 then **l** = 0 and hence describes the 1*s* orbital, of which there is only one as $\mathbf{m_l}$ = 0. Similarly, if **n** = 2 then **l** = 0 (and hence describes the 2*s* orbital, for which $\mathbf{m_l}$ = 0) or 1 (and hence describes a 2*p* orbital, for which there are **three** of them as $\mathbf{m_l}$ has three values, -1, 0 and 1).

(a) How many 3*p* orbitals can an atom have?

(b) What are the values of the three quantum numbers that must be used to describe the 3*p* orbitals?

(c) How many orbitals in total can the **n** = 3 level in an atom contain? What are they?

(d) Given that each orbital can hold a maximum of two electrons (known as the Pauli exclusion principle) the valence electron configurations for the elements He and N are $1s^2$ and $2s^22p^3$, respectively. Write valence electron configurations for the following:

(i) Be
(ii) P
(iii) Al^{3+}

A fourth quantum number must be included to describe an electron in an atom. The spin quantum number $\mathbf{m_s}$ can have the values $-1/2$ or $+1/2$ and is related to the 'spin' of an electron. If an orbital holds two electrons then they must have opposite 'spins' and hence have different $\mathbf{m_s}$ values. For example, the two valence 1*s* electrons of He can be described using quantum numbers in the following way:

electron	**n**	**l**	$\mathbf{m_l}$	$\mathbf{m_s}$
1*s*	1	0	0	$-1/2$
1*s*	1	0	0	$+1/2$

Similarly, for the valence electrons of N:

electron	**n**	**l**	$\mathbf{m_l}$	$\mathbf{m_s}$
2*s*	2	0	0	$-1/2$
2*s*	2	0	0	$+1/2$
2*p*	2	1	-1	$+1/2$
2*p*	2	1	0	$+1/2$
2*p*	2	1	1	$+1/2$

Here the three valence 2*p* electrons of N have the **same** value of $\mathbf{m_s}$ ($+1/2$ or $-1/2$); they occupy different 2*p* orbitals but have the same 'spin'. The most stable state of an atom is the one having the maximum number of unpaired electrons in any set of equivalent orbitals (known as Hund's rule). [NB: No two electrons in an atom can have the same set of four quantum numbers].

(e) Use quantum numbers to describe the valence electrons in the following:

(i) Be
(ii) P
(iii) Al^{3+}

(f) The 1st row transition metal ion Co^{3+} has six valence electrons. Write the valence electron configuration for Co^{3+} and describe the valence electrons using quantum numbers.