AUSTRALIAN CHEMISTRY OLYMPIAD

QUALIFYING EXAMINATION

1995

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
Answer **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	6.02×10^{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
Dissociation constant for water (K_W) at 25°C	10^{-14} mol^2 L^{-2}
Density of water (25°C)	997 kg m^{-3}
Density of molten wax	700 kg m^{-3}
Acceleration due to gravity	9.81 m s^{-2}
Surface tension of water (25°C)	0.072 N m^{-1}
Surface tension of molten wax	0.020 N m^{-1}

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
I	126.9	Pb	207.2	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		

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 The reaction represented by the equation

$$x\mathbf{A} + y\mathbf{B} \longrightarrow \text{products}$$

is started by mixing 1.00 mol of **A** with 2.00 mol of **B** in a 1.00 L container at a certain temperature. These concentrations are measured after a certain time.

Substance	Concentration (M)
[**A**]	0.875
[**B**]	1.81

Which is the x/y ratio in this reaction?

A 1/2

B 2/1

C 0.875/1.81

D 0.125/0.19

E 0.19/0.125

Q2 The amount of 12.3 g of $MgSO_4{\cdot}7H_2O$ is dissolved in 87.7 g of H_2O. The density of the solution is 1.06 g mL^{-1} (T=20°C). What is the molarity of the solution?

A 0.49 M

B 0.53 M

C 0.59 M

D 0.62 M

E 0.67 M

Q3 The vapour pressure of H_2O at 25°C is 23.8 mm of mercury. If 34.0 mL of O_2 are collected over water at 740 mm of mercury and 25°C, what will be the volume of dry O_2 at 0°C and 760 mm of mercury?

A 29.4 mL

B 30.3 mL

C 32.0 mL

D 33.1 mL

E 28.9 mL

Q4 Which electronic transition occurs with the greatest release of energy in a hydrogen atom?

A $n = 2 \rightarrow n = 3$

B $n = 3 \rightarrow n = 9$

C $n = 9 \rightarrow n = 3$

D $n = 3 \rightarrow n = 2$

E $n = 9 \rightarrow n = 2$

Q5 Which pair of the following elements would form a compound with 1:2 stoichiometry?

Element	Electron configuration
W	$1s^2 2s^2 2p^4$
X	$1s^2 2s^2 2p^6 3s^1$
Y	$1s^2 2s^2 2p^6 3s^2$
Z	$1s^2 2s^2 2p^6 3s^2 3p^3$

A **W** and **X**

B **W** and **Y**

C **X** and **Y**

D **Y** and **Z**

E **X** and **Z**

Q6 Which set of species is arranged in order of increasing O—N—O bond angle?

A NO_2^-, NO_2, NO_2^+

B NO_2, NO_2^-, NO_2^+

C NO_2^+, NO_2, NO_2^-

D NO_2, NO_2^+, NO_2^-

E NO_2^-, NO_2^+, NO_2

Q7 The fact that $Pt(NH_3)_2Cl_2$ exists in two different isomeric forms offers evidence that geometry is

A octahedral

B trigonal planar

C tetrahedral

D square planar

E trigonal bipyramidal

Q8 Consider this reaction at equilibrium.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^\circ = -198 \text{ kJ}$$

Which of these changes would cause an increase in the SO_3/SO_2 mole ratio?

A adding a catalyst

B removing $O_2(g)$

C decreasing the temperature

D decreasing the pressure

E none of the above

Q9 A weak monoprotic acid (25.0 mL of a 0.10 M solution) is titrated to a phenolphthalein end-point with a 0.10 M solution of NaOH. Which statement about this titration is true?

A The volume required will be less than 25.0 mL.

B The pH at the equivalence point will be less than 7.

C The solution will be colourless after 27.0 mL of NaOH have been added.

D The $[H^+] = [OH^-]$ at the equivalence point.

E The pH at the equivalence point will be above 7.

Q10 The solubility product, K_{sp}, of $PbI_2(s)$ is 1.4×10^{-8} at 25°C. What is the solubility of PbI_2 in moles per litre?

A 1.2×10^{-4}

B 1.5×10^{-3}

C 1.9×10^{-3}

D 2.4×10^{-3}

E 1.7×10^{-4}

Q11 Which is predicted to be most soluble in water?

A C_2H_6

B C_2H_5OH

C $C_2H_4Cl_2$

D $(C_2H_5)_2O$

E $(C_2H_5)_3COH$

Q12 If solid nickel metal was added to separate aqueous solutions each containing 1 M concentrations of Ag^+, Cd^{2+}, Cu^{2+} and Sn^{2+} ions, how many metals would plate out, based on the given standard reduction potentials?

Standard Reduction Potentials	
Cu^{2+}/Cu	0.16 V
Ag^+/Ag	0.799 V
Sn^{2+}/Sn	–0.141 V
Ni^{2+}/Ni	–0.236 V
Cd^{2+}/Cd	–0.400 V

A zero

B one

C two

D three

E four

Q13 Use the given bond energies and the equation to calculate the H—F bond energy in kJ mol^{-1}.

$$H_2(g) + F_2(g) \longrightarrow 2HF(g) \qquad \Delta H = -541 \text{ kJ}$$

Bond Energies ($kJ\ mol^{-1}$)	
H_2	436
F_2	153

A 1130

B 48

C 565

D 294.5

E 24

Q14 Given the acids and their K_a values listed in the following table, which sequence lists the corresponding anions in order of base strength?

Equilibrium values for K_a at 25°C	
$HC_2H_3O_2$	1.8×10^{-5}
HCN	6.2×10^{-10}
HF	7.2×10^{-4}

A CN^-, $C_2H_3O_2^-$, F^-

B $C_2H_3O_2^-$, CN^-, F^-

C F^-, $C_2H_3O_2^-$, CN^-

D F^-, CN^-, $C_2H_3O_2^-$

E CN^-, F^-, $C_2H_3O_2^-$

Q15 Among the compounds below select those from which propyl butanoate would be synthesised under favourable reaction conditions and reaction yield.

a $CH_3CH_2CH_2CONH_2$
b H_2SO_4
c CH_3CH_2COCl
d $CH_3CH_2CH_2COOH$
e $CH_3CH_2CH_2CH_2OH$
f $CH_3CH_2CH_2COOCOCH_2CH_2CH_3$ (acetic anhydride)
g $CH_3CH_2CH_2OH$

A c, d

B c, e

C e, g

D a, b, c

E b, d, g

SECTION B
Answer any three (3) 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

When water contacts with glass it wets the surface, travelling as a thin film. If a glass tube with a thin bore down the centre (a capillary tube) is placed vertically in a container of water (see Figure 1) the water will wet the inside. The meniscus will become concave as the thin film of water travels up the inside surface of the capillary. The requirement for the meniscus to keep its hemispherical shape pulls a column of water up the capillary tube behind it. The pressure acting at the base of the meniscus to pull this column of water up is given by the general equation;

$$P = \frac{2\gamma}{r}$$

where, γ is the surface tension of the liquid, in this case water. The water will continue to rise until the weight of the water above the water level in the container exerts a pressure equal and opposite to the pressure due to the surface tension.

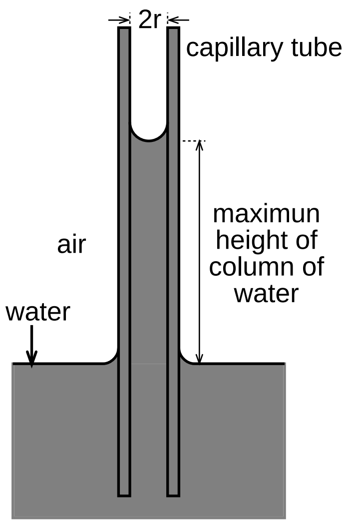


Figure 1

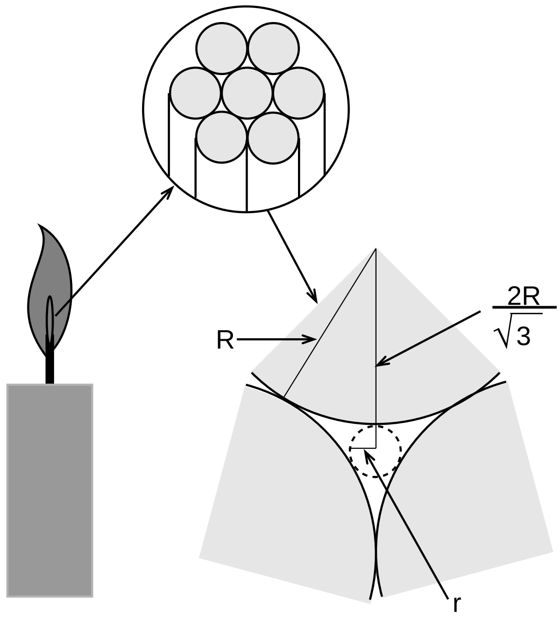


Figure 2

(a) For a capillary tube 0.4 mm in diameter how high would you expect the water to rise?

(b) (i) A bundle of fibres can also provide a system of capillaries for the transport of liquids. A good example is given in Figure 2 where the tubular space between the fibres of a candle wick can transport molten wax up to a flame. The capillary tubes in this case can be given an approximate radius, r. If the radius, R, of an average fibre is 0.05 mm then what would be the longest candle wick possible?

(ii) Why is this height never attained in practice?

(c) Name two systems where capillary transport of fluids is important.

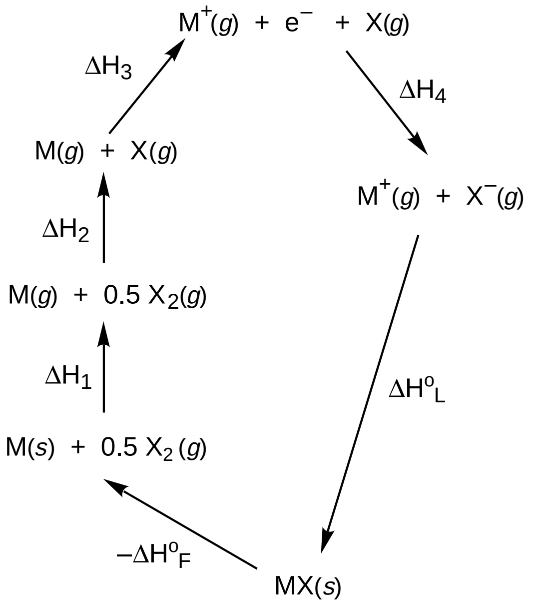
Q17

Lattice energy (ΔH^o_L) can be defined as the energy change that occurs when gaseous ions are packed to form an ionic solid ie. $M^+(g) + X^-(g) \rightarrow MX(s)$. Lattice energy is always exothermic and hence has a negative sign. It is directly proportional to the product of the numerical charges of the ions and inversely proportional to the internuclear distance, **d**, between neighbouring oppositely charged ions.

(a) Given that LiCl and SrO have the same structure and similar values of **d**, which would be expected to have the larger lattice energy and by how much?

(b) Arrange the following ionic compounds in order of increasing lattice energy: KBr, NaF, $MgBr_2$, KF and MgF_2.

Theoretical values of lattice energy can be used to determine the enthalpy of formation (ΔH^o_F) of an ionic solid (eg. MX) using a thermochemical cycle known as a **Born-Haber cycle**:



According to Hess's law $\sum \Delta H = 0$ in a thermochemical cycle,

ie. $-\Delta H^o_F + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H^o_L = 0$

where
ΔH^o_F = enthalpy of formation of MX(s);
ΔH_1 = enthalpy of sublimation of M(s);
$\Delta H_2 = 0.5\ D(X_2)$ {$D(X_2)$ is the bond dissociation energy for X_2};
ΔH_3 = ionisation energy for $M(g) \rightarrow M^+(g) + e^-$;
ΔH_4 = electron affinity for $X(g) + e^- \rightarrow X^-(g)$; and
ΔH^o_L = lattice energy of MX(s).

Table 1		
Lattice energy	–911 kJ mol^{-1} (NaF)	–2910 kJ mol^{-1} (MgF_2)
1st ionisation energy	496 kJ mol^{-1} (Na)	738 kJ mol^{-1} (Mg)
2nd ionisation energy	4560 kJ mol^{-1} (Na)	1450 kJ mol^{-1} (Mg)
Enthalpy of sublimation	108 kJ mol^{-1} (Na)	141 kJ mol^{-1} (Mg)
Electron affinity	–332 kJ mol^{-1} (F)	
Bond dissociation energy	155 kJ mol^{-1} (F_2)	

(c) Construct a Born-Haber cycle for NaF(s) and determine the enthalpy of formation (ΔH^o_F) using the data in Table 1.

(d) Repeat the exercise for $MgF_2(s)$ using the data in Table 1.

(e) With reference to the data given in Table 1, explain why magnesium reacts with fluorine to give $MgF_2(s)$ and not MgF(s) whereas sodium forms NaF(s) and not $NaF_2(s)$?

Q18

(a) The volumetric analysis of lead can be accomplished by an indirect process which involves chromate ion and iodine.

The lead, as Pb^{2+}, is initially treated with excess chromate ion (CrO_4^{2-}) to yield insoluble lead chromate.

Write a balanced equation for this reaction.

(b) The lead chromate is isolated and dissolved in hydrochloric acid to afford lead chloride and dichromate ion ($Cr_2O_7^{2-}$), which is present as $H_2Cr_2O_7$.

Write a balanced equation representing the reaction of CrO_4^{2-} with H^+ to afford $Cr_2O_7^{2-}$

(c) and hence

Write a balanced overall equation for the reaction of lead chromate with HCl.

(d) In acidic solution $Cr_2O_7^{2-}$ reacts with iodide to yield Cr^{3+} and iodine.

Write half equations for the reduction of dichromate ion and the oxidation of iodide ion.

(e) Using all the above information show that 1 mole of Pb^{2+} ultimately liberates $^3/_2$ moles of iodine.

(f) Iodine can be determined by reaction with thiosulfate, a reaction which reduces iodine to iodide and oxidises thiosulfate ($S_2O_3^{2-}$) to dithionate ($S_4O_6^{2-}$).

Using the half equation method deduce a balanced equation for the reaction of iodine with thiosulfate, and hence show that overall 1 mL of 1 M $Na_2S_2O_3$ equates to 0.06907 g of Pb^{2+}.

(g) A sample of technical grade PbO (1.000 g) was analysed **via** its chromate and the solution containing the $H_2Cr_2O_7$ diluted to a final volume of 200.0 mL, with distilled water. A 25.0 mL sample of this solution was reacted with an excess of potassium iodide. The liberated iodine required 15.57 mL of 0.1050 M $Na_2S_2O_3$ to achieve an endpoint to the titration.

What was the % by weight of lead in the original sample of PbO?

(h) What was the % purity of the PbO?

(i) What indicator might reasonably have been used to detect the endpoint in the iodine/thiosulfate titration?

(j) In general what elements will interfere with this analysis for lead?

(k) Name one specific element which will interfere with the analysis.

Q19

Modern organic chemistry has benefited greatly from the development of spectroscopy. Relative molecule masses can routinely be determined by mass spectrometry and carbon n.m.r. (nuclear magnetic resonance) spectroscopy provides a detailed picture of the bonding between carbon and hydrogen and also the molecular environment in which carbon atoms are found. The following problem illustrates how these techniques may be used in solving structural problems.

(a) A young chemistry student was confronted by a Professor who presented her with a phial containing an unidentified compound and naturally enough, wanted to know the identity of the unknown compound. Full of enthusiasm the young chemist set to work and quickly found that the mysterious compound contained 64.27% C; 7.19% H and that the rest was oxygen. She then wrote down an **empirical formula** for her unknown.

What was the empirical formula the chemist derived?

(b) With the aid of a mass spectrometer our young chemist determined that the **relative molecular mass** of the unknown compound was 112. A quick calculation provided the **molecular formula**.

What was the molecular formula of the unknown?

(c) Flushed with success she spent a long and largely fruitless night writing out possible structure using every functional group she could think of.

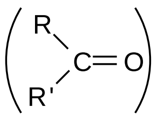
Draw one structure which fits the molecular formula and which contains

(i) an alcohol

(ii) an ether

(iii) a carboxylic acid

(d) By dawn it was clear that this wasn't going to yield a quick result and our chemist recorded a carbon n.m.r. spectrum. Immediately two facts became clear. Firstly her molecule contained at least one **carbonyl group**



and secondly that the molecule was symmetrical about a plane through the centre. This data limited the number of possible structures.

Draw three structures which fit all the data available to date, and name the functional groups present in your answer.

(e) Another hour's work and the chemist had her answer, for she could see in the carbon n.m.r. spectrum that the molecule contained in addition to carbonyls, only CH_3, and CH groups. Furthermore the CH groups contained carbons that were sp^2 hybridised.

(i) What was the structure of the unknown molecule.

(ii) What was the systematic IUPAC name for this molecule.

(f) Full of pride she rushed to inform her Professor of the result. " Well done," said the Prof., " it was easy wasn't it?" " Yes," said the young enthusiast, " it was." " Try this one then," said the Prof., " it's **isomeric** with your first unknown, it's **cyclic**, contains both an **aldehyde** and a **ketone** and has only one **methylene** (CH_2) **group**." " Easy," said the young chemist and proceeded to write the structure on the Prof's white board.

What was the structure she wrote.

(g) " I would only give 50% for that answer," said the Prof., " as you have overlooked one important consequence of the molecular shape." As was nearly always the case, the Prof was right.

Suggest what the young chemist had overlooked in her haste to provide a structure for the second unknown compound?