



CHEMISTRY

KEY

Higher Level

Sectin.

Thursday 6 May 1999 (afternoon)

Paper 2

2 hours 15 minutes

A

Candidate name:	Candidate category & number:							

This examination paper consists of 2 sections, Section A and Section B.

The maximum mark for Section A is 40.

The maximum mark for Section B is 50.

The maximum mark for this paper is 90.

INSTRUCTIONS TO CANDIDATES

Write your candidate name and number in the boxes above.

Do NOT open this examination paper until instructed to do so.

Section A: Answer ALL of Section A in the spaces provided.

Section B: Answer TWO questions from Section B. You may use the lined pages at the end of this paper or attach extra sheets of paper with your candidate number clearly marked at the top.

At the end of the examination, complete box B below with the number of the questions answered in Section B.

B

QUESTIONS ANSWERED	
A/ ALL	
B/	
B/	
Number of extra sheets attached	

C

EXAMINER	MODERATOR
/40	/40
/25	/25
/25	/25
TOTAL /90	TOTAL /90

D

IBCA
/40
/25
/25
TOTAL /90

EXAMINATION MATERIALS

Required:

Calculator

Chemistry Data Booklet

Millimetre square graph paper

Allowed:

A simple translating dictionary for candidates not working in their own language

SECTION A

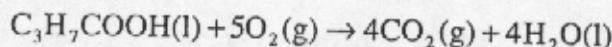
Answer ALL questions.

In order to receive full credit in Section A, the method used and the steps involved in arriving at your answer must be shown clearly. It is possible to receive partial credit but, without your supporting work, you may receive little credit. For numerical calculations, you are expected to pay proper attention to significant figures.

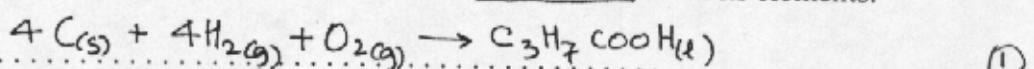
1.

Substance	Standard Enthalpy of Formation, ΔH_f° / kJ mol ⁻¹	Absolute Entropy, S° , / J mol ⁻¹ K ⁻¹
C(s)	0.0	5.7
CO ₂ (g)	-393.5	213.6
H ₂ (g)	0.0	130.6
H ₂ O(l)	-285.9	69.9
O ₂ (g)	0.0	205.0
C ₃ H ₇ COOH(l)		226.3

The enthalpy change for the combustion of butanoic acid at 25° C is -2183.5 kJ mol⁻¹. The combustion reaction is:



- (a) Write the balanced equation for the formation of butanoic acid from its elements. [1]



(read states for mark)

- (b) Using the above data, calculate the standard enthalpy of formation, ΔH_f° , for butanoic acid. [3]

$$\begin{aligned} \Delta H_{rxn}^\circ &= \sum \Delta H_{fP}^\circ - \sum \Delta H_{fR}^\circ \quad \text{(1)} \\ \therefore -2183.5 \text{ kJ} &= [4(-393.5) + 4(-285.9)] - [\Delta H_f^\circ + 5(0)] \quad \text{(1)} \\ &= [(-1574) + (-1143.6)] - \Delta H_f^\circ \\ &= -2717.6 - \Delta H_f^\circ \end{aligned}$$

$$\begin{aligned} \therefore \Delta H_f^\circ &= (2183.5 \text{ kJ} - 2717.6) \text{ kJ} \\ &= -534.1 \text{ kJ} \quad (\text{or kJ mol}^{-1}) \end{aligned}$$

can be
implicit
in step 2.

(This question continues on the following page)

(Question 1 continued)

- (c) Calculate the standard entropy change, ΔS° , for the formation of butanoic acid at 25° C. [3]

$$\begin{aligned}\Delta S^\circ &= \sum S_p^\circ - \sum S_R^\circ = S_{\text{CH}_3\text{COOH}}^\circ - (S_{\text{C}_2\text{H}_5\text{CH}_2}^\circ + 4S_{\text{H}_2}^\circ + 2S_{\text{O}_2}^\circ) \quad (1) \\ &= (226.3) - [4(57) + 4(130.6) + (205.0)] \text{ J mol}^{-1} \text{ K}^{-1} \quad (1) \\ &= -523.9 \frac{\text{J}}{\text{mol K}} - 0.5239 \frac{\text{kJ}}{\text{mol K}} \quad (1)\end{aligned}$$

If units in (b) & (c) are wrong/omitted penalise by 1 mark (0-1)

- (d) Calculate the standard free energy of formation, ΔG_f° , for butanoic acid at 25° C. [2]

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \quad (\text{can be implicit in next step}) \\ &= -534.1 \frac{\text{kJ}}{\text{mol}} - 298\text{K}(-0.5239 \frac{\text{kJ}}{\text{mol K}}) \quad (1)\end{aligned}$$

(no double jeopardy
if ΔH or ΔS incorrect)

- (e) Is this reaction spontaneous at 25° C? Explain your answer. [1]

Since ΔG° is negative, it is spontaneous at 25° C. (1)

(no double jeopardy
if $\Delta G = +$ in d;
then non-spontaneous)

(Answers to (b), (c), (d) must be
consistent with (e) for full marks)

2. (a) $C_{20}H_{41}OH$ is the formula of an alcohol.

- (i) State and explain whether the alcohol is a solid, liquid or a gas at room temperature. [2]

A solid (no mark for liquid)

①

Relatively large vander Waal's / intermolecular forces

①

because of the very large size of the R group

①

(must have some discussion of bonding forces)

- (ii) Dodecanol is only slightly soluble in water. Explain this property. [2]

The large number of C-C and C-H bonds

①

OR the long non-polar chain

Outweighs the polar -OH (responsible for

①

H-bonding with water)

→ comments in brackets not required to score mark

- (b) The BF_3 molecule has a trigonal plane (planar triangle) shape while the NF_3 molecule is a trigonal pyramid (triangular pyramid). Explain this difference. [2]

$B-F$: BF_3 has (only) three pairs of electrons

①

around central B atom (arranged as far apart as

①

possible, thus trigonal planar)

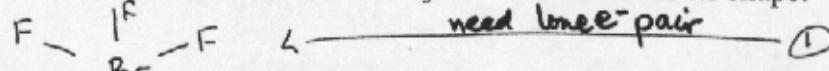
$N-F$: NF_3 has four pairs of electrons (3 bonded + 1 lone pair)

①

around central N atom

OR explanation in terms of sp^2/sp^3

- (c) Draw a diagram that represents the correct geometry of the BrF_5 molecule and state its shape. [2]



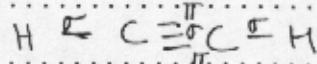
①

F — $\begin{matrix} F \\ | \\ O \\ | \\ F \end{matrix}$ — F Square pyramidal

①

OR "based on octahedral" type of argument

- (d) Give the number and types of bond between the two carbon atoms in a C_2H_2 molecule. [2]



①

one (sp) σ bond

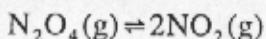
and two π bonds

①

(only 1 mark if answer is: triple bond)
or $1\sigma/2\pi = 1$

If "double", then 0.

- 3 Dinitrogen tetroxide, N_2O_4 , decomposes endothermically according to the following equation:



- (a) Give the equilibrium constant expression, K_c , for the above reaction.

[1]

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} ; \text{ need square brackets for mark}$$

- (b) 1 mol of N_2O_4 was placed in a 1.00 dm^3 evacuated flask at 25° C . The flask was stoppered and equilibrium was allowed to be established at this temperature. State whether the yield of NO_2 will increase, decrease, or remain the same when equilibrium is re-established after each of the following independent changes. Give a brief explanation in each case.

- (i) More N_2O_4 is added to the equilibrium mixture in the flask.

[2]

$[\text{NO}_2]$ increases or yield decreases

(1)

Equilibrium is disturbed; shifts to the right to use up

(1)

Some of the N_2O_4 added (Le Chatelier's principle).

OR Since $[\text{NO}_2]$ increases and K_c is constant ($[\text{NO}_2]$ increases)

- (ii) The pressure on the system is increased.

[2]

$[\text{NO}_2]$ decreases or yield decreases

(1)

Increased P favours smaller volume, thus equilibrium shifts to the left.

(1)

- (iii) A catalyst is added to the system.

[2]

$[\text{NO}_2]$ is unchanged or yield unchanged

(1)

Catalyst affects both forward and backward rxns equally

(1)

OR Catalyst does not affect position of equilibrium because ...

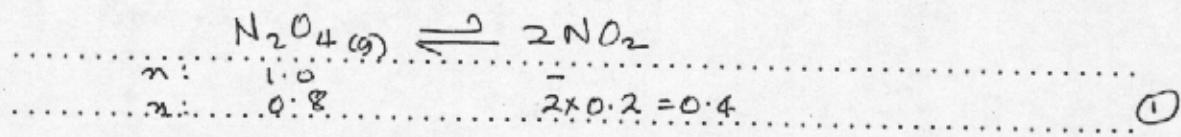
(Question 3 continued)

- (c) The 1 mol of N_2O_4 in the flask at 25°C became 0.8 mol of N_2O_4 when equilibrium had been established.

Calculate;

- (i) the mols of NO_2 present at equilibrium.

[1]



①

- (ii) the numerical value of K_c with its units.

[2]

$$K_c = \frac{(0.4)^2}{0.8} = 0.2 \text{ mol dm}^{-3}$$

①

①

- (d) State and explain the effect on the value of K_c if the temperature of the reaction were raised to 100°C .

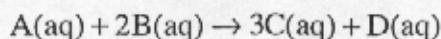
[2]

Forward reaction is endothermic, forward rxn favoured (or equilibrium move to the right) to use up some of the heat provided

∴ K_c increases.

①

The following data were obtained for the reaction between A and B:



Experiment	Initial concentration of Reactants (mol dm^{-3})		Initial Rate of Reaction ($\text{mol dm}^{-3} \text{ hr}^{-1}$)
	A	B	
1	0.200	0.200	0.50
2	0.400	0.200	2.00
3	0.400	0.800	8.00

[A] doubles, rate up by 4
∴ rate $\propto [A]^2$

- (a) Give the order with respect to A.

2

1 ①

[1]

- (b) Give the order with respect to B.

1

1 ①

[1]

- (c) Write the rate expression for this reaction.

$$\text{rate} = k[A]^2[B]^1 \quad ; \quad \text{need sq. brackets for marks}$$

1 ①

- (d) Using the data from the first experiment, calculate the value of the rate constant and give its units.

no double jeopardy if ① is incorrect

$$0.50 \frac{\text{mol}}{\text{dm}^3 \text{ h}} = k(0.2)^2(0.2) \frac{\text{mol}^3}{\text{dm}^9}$$

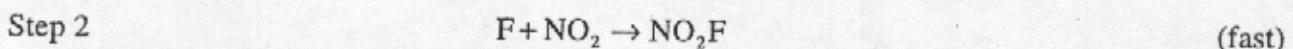
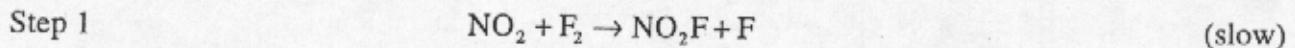
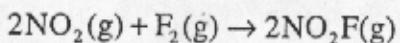
$$\therefore k = 62.5 \text{ (dm}^6 \text{ mol}^{-2} \text{ h}^{-1}\text{)}$$

[1]

[1]

1 ①

5. Evidence suggests that reaction between the gases nitrogen dioxide and fluorine is a two-step process:



- (a) State and explain which step is the rate determining step. [1]

Step 1 since it is the slow step.

(need explanation for mark)

- (b) State and explain which of the two steps is expected to have the higher activation energy. [2]

Step 1

It is the slow step, therefore has a higher activation energy compared to step 2.

- (c) Give the rate expression of the reaction based on your answer to (a). [1]

rate = $k[\text{NO}_2][\text{F}_2]$; need 3 for mark

(no double jeopardy if answer in (a) is incorrect,

then accept appropriate answer.)

SECTION B

Answer TWO of the questions in this section. You may use the lined pages at the end of this paper or attach extra sheets of paper with your candidate number clearly marked at the top.

6. Use the modern theory of the atom to answer each of the following.

- (a) List the *d*, *f*, *p* and *s* orbitals in order of **increasing** relative energy. [2]
- (b) Give the **number** of each type of orbital, *d*, *f*, *p* and *s* at each energy level. [2]
- (c) Describe the changes which occur when hydrogen produces a line spectrum. [2]
- (d) Explain why the electron configuration of the nitrogen atom is written as N: $1s^2 2s^2 2p^1 2p^1$ rather than N: $1s^2 2s^2 2p^2 2p^0$.
Write the electron configuration of titanium. [3]
- (e) (i) Name the instrument used to determine the atomic masses of the two naturally occurring isotopes of gallium. Briefly describe each step involved in the operation of the instrument. [6]
- (ii) A certain sample of gallium contains 60 % Ga-69 and 40 % Ga-71. Give the nuclear structures of these isotopes and calculate the relative atomic mass of gallium in this sample. [4]
- (f) Explain the difference in the two values of ionisation energy for each of the following pairs: [6]
- (i) the 1st ionisation energy of beryllium is 900 kJ mol^{-1} whereas the 2nd ionisation energy of beryllium is 1757 kJ mol^{-1} .
- (ii) the 1st ionisation energy of aluminium is 577 kJ mol^{-1} whereas the 1st ionisation energy of magnesium is 736 kJ mol^{-1} .
- (iii) the 1st ionisation energy of aluminium is 577 kJ mol^{-1} whereas the 1st ionisation energy of boron is 799 kJ mol^{-1} .

7. This question is concerned with acids and bases.

- (a) Some of the active ingredients in commercial antacids are NaHCO_3 , $\text{Al}(\text{OH})_3$, and CaCO_3 .
- (i) Explain why NaHCO_3 could be described as both a Brønsted-Lowry base and a Lewis base. Which of these two descriptions applies to CaCO_3 ? [3]
- (ii) Write balanced equations showing the reactions that occur when excess stomach acidity, represented by the formula HCl , is decreased by each antacid. [4]
- (iii) Calculate the number of moles of antacid present in 1 gram of each sample and hence compare their neutralising power. [6]
- (iv) Give **two** reasons why these antacids are used in preference to sodium hydroxide. [2]
- (b) Zinc hydroxide is a white solid that reacts with both strong acids and strong bases.
- (i) What name is given to this type of behaviour? [1]
- (ii) Write ionic equations for the reaction of zinc hydroxide with strong acid and strong base. Give another example of a compound which exhibits this behaviour. [5]
- (iii) Define a Lewis acid. Explain why transition metal ions can function as Lewis acids and give an equation to support your answer. [4]

8. (a) (i) Use the data in the table below to identify the type of bonding in each of the chlorides listed and state how the given properties depend on the type of bonding. Support your answer with appropriate diagrams. [9]

Chloride	m.p. /K	b.p. /K
Sodium chloride	1074	1686
Aluminium chloride	451 sublimes	
Phosphorus(III) chloride	161	349

- (ii) Describe how the chlorides behave when added to water. Give equations for any reactions which occur. [5]
- (b) (i) State the bonding in the oxides of sodium, magnesium, silicon and phosphorus. [4]
- (ii) What happens to the pH of pure water when these oxides are added to separate samples of the water? Give equations for any reactions which occur. [7]

- (a) A compound **C** with an empirical formula of $C_4H_{10}O$ has a mass spectrum which includes peaks at 74 and 59 and an infrared spectrum with a band at $3230\text{--}3350\text{ cm}^{-1}$. Use this data to;
- (i) determine, with reasoning, the molecular formula of **C**. [2]
- (ii) account for the peak at 59. [1]
- (iii) identify the functional group giving the band at $3230\text{--}3350\text{ cm}^{-1}$. [1]
- (b) **C** reacts with acidified dichromate(VI) to produce an organic acid. Give the **two** possible structural formulae of **C**. [2]
- (c) When **C** is dehydrated it gives a compound **D** which has an infrared spectrum with a band at $1620\text{--}1680\text{ cm}^{-1}$. Use this data to;
- (i) identify the functional group present. [1]
- (ii) give **two** possible structural formulae of **D**. [2]
- (iii) give the **four** possible structures of the compound formed when **D** reacts with hydrogen chloride. [3]
- (d) **D** actually forms **E**, $CH_3C(Cl)(CH_3)CH_3$, when it reacts with hydrogen chloride. Which structural formulae of **D** produces **E**? [1]
- (e) **E** is hydrolysed with OH^- ions to produce **F** by an S_N1 mechanism.
- (i) What is meant by an S_N1 mechanism? [3]
- (ii) Why does an S_N1 rather than an S_N2 mechanism occur? [3]
- (iii) Give the stepwise mechanism for the conversion of **E** to **F**. [5]
- (f) State and explain whether or not **F** reacts with acidified dichromate(VI). [1]

[2 marks]

SECTION B

- Answer TWO of the questions in this section. You may use the lined pages at the end of this paper or attach extra sheets of paper with your candidate number clearly marked at the top.
6. (a) s, p, d, f
 p, s, f, d deduct 1 mark
 g marks

- (b) $d = 5, f = 7, p = 3, s = 1$
- 4 correct [2 marks]
 2 or 3 correct [1 mark]
 1 correct [0 marks]

(c) { electrons move (to lower) energy levels/orbitals

emitting energy as they do so
ex citatiōn and/or promotion to higher energy level

- [2] (d) Fill singly before doubling
 since two electrons in the same orbital will repel



- [2] (e) (i) Mass spectrometer.
 A sample of naturally occurring gallium vapour is injected into the evacuated ionising chamber where an electron beam ionises a part of the sample by knocking electrons from the neutral atoms or molecules.

- Charged plates accelerate the positive ions towards the detector and the ions pass through a magnetic field perpendicular to their path where the charged ions are separated (deflected) into different paths.
 The detector detects the paths according to the masses of the particles. **Accept labelled diagram + adequate explanation.**

Any five points from the six given. [max 6 marks]

- [6] (f) Explain why the electron configuration of the nitrogen atom is written as

N: $1s^2 2s^2 2p^1 2p^1$ rather than N: $1s^1 2s^2 2p^2 2p^0$. Write the electron configuration of titanium.

- [4] (g) Name the instrument used to determine the atomic masses of the two naturally occurring isotopes of gallium. Briefly describe each step involved in the operation of the instrument.

- [6] (h) A certain sample of gallium contains 60 % Ga-69 and 40 % Ga-71. Give the nuclear structures of these isotopes and calculate the relative atomic mass of gallium in this sample.

- [4] (i) Explain the difference in the two values of ionisation energy for each of the following pairs:

- (i) the 1st ionisation energy of beryllium is 900 kJ mol^{-1} whereas the 2nd ionisation energy of beryllium is 1757 kJ mol^{-1} .

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- (iii) the 1st ionisation energy of aluminium is 577 kJ mol^{-1} whereas the 1st ionisation energy of boron is 799 kJ mol^{-1} .

- [6] (j) (i) removed from a positively charged ion, Be^+ (g), whereas the first electron is removed from a neutral atom, $\text{Be}(g)$.
1st electron is removed from a full sub-orbital; 2nd electron is removed from a singly occupied sub-orbital, gains 1 mark only

- (ii) Electron from 3p in Al but electron from 3s in Mg which is of lower energy

- (iii) Electron from $2p$ in B] "p" not essential
 Electron from 4p in Al

- The latter is further from the nucleus / the former is nearer to the nucleus

Total [25 marks]

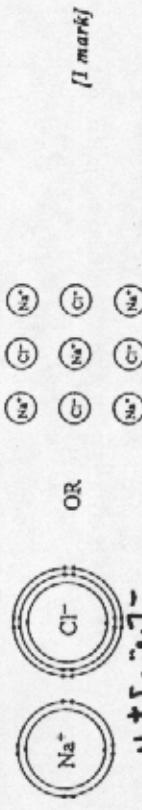
Turn over

- (a) (i) Use the data in the table below to identify the type of bonding in each of the chlorides listed and state how the given properties depend on the type of bonding. Support your answer with appropriate diagrams.

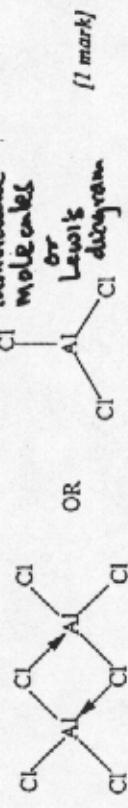
Chloride	m.p./K	b.p./K
Sodium chloride	1074	1686
Aluminium chloride	451 _{sublimates}	
Phosphorus(III) chloride	161	349

- (a) (ii) Describe how the chlorides behave when added to water. Give equations for any reactions which occur.
- (b) (i) State the bonding in the oxides of sodium, magnesium, silicon and phosphorus.
- (ii) What happens to the pH of pure water when these oxides are added to separate samples of the water? Give equations for any reactions which occur.

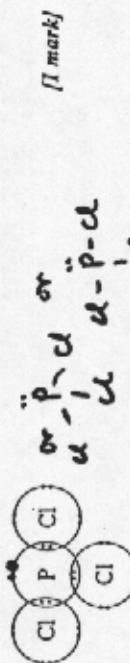
8. (a) (i) NaCl – high melting and boiling points – giant structure/ionic
- strong attraction between ions



- (b) (i) Al_2Cl_6 – low melting and boiling points – simple molecular/covalent
- associated or weak forces between individual Cl molecules

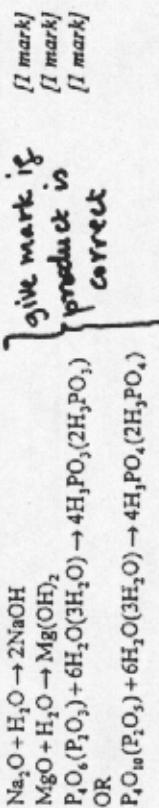


- (b) (ii) PCl_3 – low melting and boiling points – simple molecular/covalent
- weak forces between individual molecules



- (b) (iii) NaCl dissolves. **Caution accept dissociates** AlCl₃, vigorous reaction with ~~water~~ ~~gives~~ gas evolved
PCl₃ gives vigorous reaction with ~~water~~ ~~gives~~ " fumes "
 $\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})_3 + \text{HCl}$
 $\text{PCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3 + 3\text{HCl}$

- (b) (iv) (i) ionic, **covalent**, covalent
(ii) strong alkali, weak alkali, nothing, acid
OR OR OR OR OR
high pH pH above 7 7 below 7



Total [25 marks]

