G.C.E. (A/L) Examination 2006 April
Chemistry II / Three hours

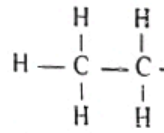
- Periodic Table is provided.
- Use of calculators is not allowed.

PART A - Structured Essay (Pages 2-8)

- Answer all the questions.
- Write your answer in the space provided for each question. Please note that the space provided is sufficient for the answer and that extensive answers are not expected.

N.B. INSTRUCTION BOX

In answering questions 3 and 4, you may represent alkyl groups in a condensed manner.

e.g.  may be shown as CH_3CH_2 -

PART B and PART C - Essay (pages 9-12)

Answer **four** questions selecting two questions from each part. Use the paper supplied for this purpose.

At the end of the time allotted for this paper, tie the answers to three parts **A**, **B** and **C** together so that Part **A** is on top and hand them over to the Supervisor.

You are permitted to remove only Parts **B** and **C** of the question paper from the Examination Hall.

Universal gas constant, R	= 8.314 $JK^{-1} mol^{-1}$
Avogadro constant N_A	= 6.022 x 10^{23} mol^{-1}

PART A - STRUCTURED ESSAY

Answer **all four** questions. Each question carries **10 marks.)**

1. (a) Complete the following statements :

(i) The element with the highest melting point among Li, Na and Mg is .....

(ii) The element that reacts most vigorously with water among Li, Na and K is .....

(iii) The most thermally stable carbonate among Na_2CO_3, $CaCO_3$ and $MgCO_3$ is .....

(iv) The most water soluble hydroxide among $Mg(OH)_2$, $Ca(OH)_2$ and $Ba(OH)_2$ is .....

(v) The two elements that show the **same highest** oxidation state among Cl, Mn, P and Cr are ..... and .....

(3.0 marks)

(b) The element **M** reacts easily with dilute H_2SO_4 as well as with dilute aqueous NaOH solution at room temperature liberating the same gas. The salts of **M** are not electron deficient compounds.

Identify **M** .....

Write balanced chemical equations for the reactions of **M** with (i) dil. H_2SO_4 (ii) aqueous NaOH.

(i) .....

(ii) .....

Give **one** industrial application of **M**.

.....

(2.5 marks)

(c) (i) Write the resonance structures of the N_3^- (azide) ion.

.....

.....

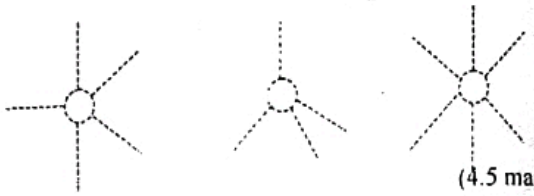
Give **one** application you have read or heard about of sodium azide.

.....

(ii) Three sketches that can be used to show the arrangements of repulsion units (bonds and lone pairs) in molecules are given below. Indicate the arrangement of the repulsion units around the central atom in the molecules.

SiF_4, XeF_4, and SF_4

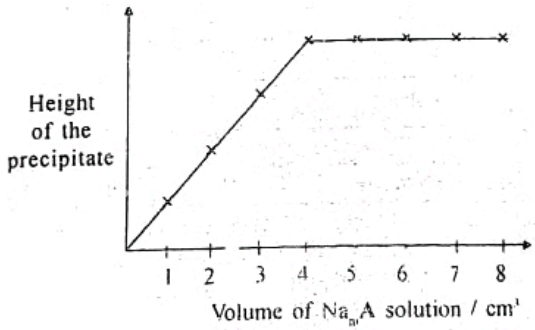
by choosing the appropriate sketch. For this purpose indicate the central atom inside the circle, bonds by solid lines (-) and lone pairs by



(4.5 marks)

2. (a) MCl_n and Na_mA are two water soluble salts. Aqueous solutions of these react together forming an immediate precipitate M_mA_n

In an experiment to determine the stoichiometry of this reaction, 9 cm^3 portions of 0.2 mol dm^{-3} MCl_n solution were mixed, in test tubes, with varying volumes of 0.3 mol dm^{-3} Na_mA solution, and the height of the precipitate after the precipitate had settled down, was measured. The results are given in the following graph.



(i) Deduce the stoichiometry of the reaction.

.....

.....

.....

.....

.....

(ii) Is the above method suitable for determining the stoichiometry of the reaction between $Al_2(SO_4)_3$ and NH_4OH?

Yes / No (Delete the inappropriate word)

Give **two** reasons to support your answer.

.....

.....

(5.0 marks)

(b) The ester $R-\overset{O}{\overset{\|}{C}}-OR_2$ is a crystalline solid. R_1 and R_2 are hydrocarbon chains. This ester undergoes hydrolysis to give the following equilibrium.

$$R_1COOR_2(s) + H_2O(\ell) \rightleftharpoons R_1COOH(aq) + R_2OH(aq)$$

The statements given below refer to a procedure for the hydrolysis of the ester. Fill in the blanks in the statements using only suitable words/phrases, selected from the list given below. The same word/phrase may be used more than once. Each blank should be filled with one word only.

List of words/ phrases to be used :

activation energy, boiling - point, carboxylic acid, catalysts, concentration, contact, decreases, density, equilibrium, increases, left, mixing, organic compound, rate, right, slowly, sodium salt, solid, yield.

(i) The ester is ground to a fine powder.

Grinding ..... the surface area of the solid This leads to an increase in the ..... between reactants.

(ii) The rate of hydrolysis can be increased by using acids or bases. Hydrolysis by water alone occurs ..... due to the high .... of the reaction. Acids and bases act as ..... for this reaction.

(iii) Aqueous NaOH is more suitable than aqueous HCl for the above hydrolysis. Acid hydrolysis gives an ..... mixture of products and reactants. Hence the amount of product obtained is limited by the ..... concentrations. When base is used, the carboxylic acid formed on hydrolysis is removed from the ..... mixture as the .... The equilibrium is thus pushed to the ..... and the ..... is increased.

(iv) The powdered ester is stirred with dil. NaOH and heated to 60°C to complete the hydrolysis. Stirring helps to increase ..... between reactants and heating increases the ..... of the reaction.

(v) After complete hydrolysis, when excess NaCl is dissolved in the reaction mixture, a white solid separates and rises to the top.

Dissolved NaCl increases the ..... of ions in solution. Under these conditions the less soluble .... of the carboxylic acid separates. As the dissolved NaCl also increases the ..... of the solution, the solid rises to the top.

(5.0 marks)

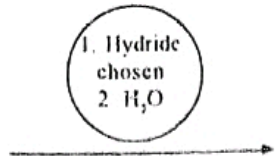
3. Selecting appropriate reagents and solvents for the chemical reactions involved only from the following list, answer parts (a) and (b).

acetone (CH_3COCH_3), aniline ($C_6H_5NH_2$),
bromobenzene(C_6H_5Br), toluene ($C_6H_5CH_3$)
Mg, Fe,Pt
Br_2, PCl_5, NaCN cuprous bromide (Cu_2Br_2), $AlCl_3$, CH_3Cl
$NaBH_4$, $LiAlH_4$ $KMnO_4$, $NaNO_2$
conc.HNO_3, conc. H_2SO_4
aq. NaOH, dil. H_2SO_4
water, ethanol (C_2H_5OH), ether ($C_2H_5OC_2H_5$)

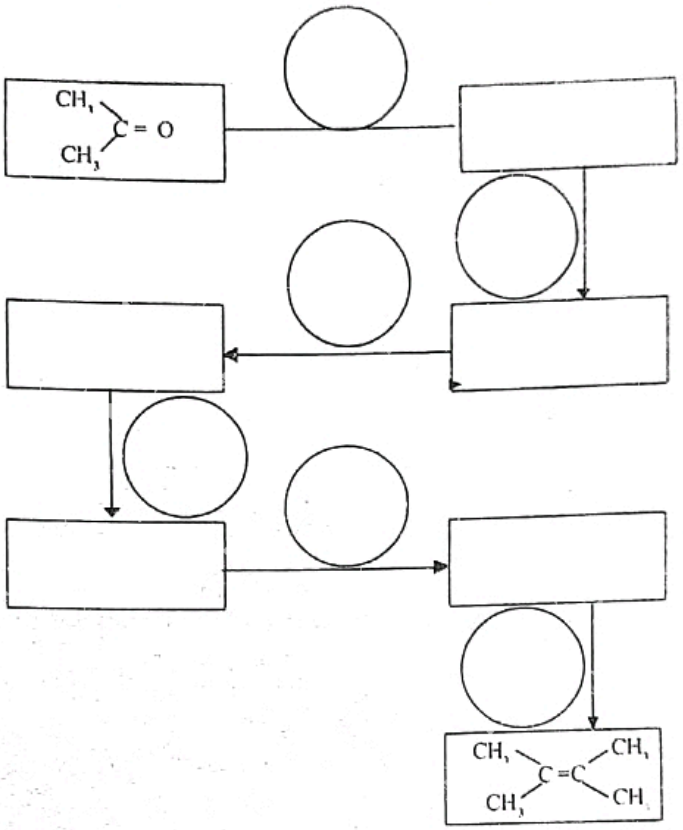
Note :

(I) **In the following schemes, write in the boxes the structures of the appropriate compounds and in the circles the appropriate reagents / solvents.**

(II) **Each arrow indicates a single reaction except in the case of hydride reduction followed by hydrolysis for which the reagents should be given in the same circle as shown below.**

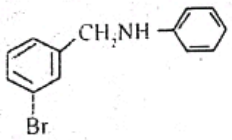


(a) Show how you would prepare 1,1,2, 2- tetramethylethene from acetone by completing trh scheme given below

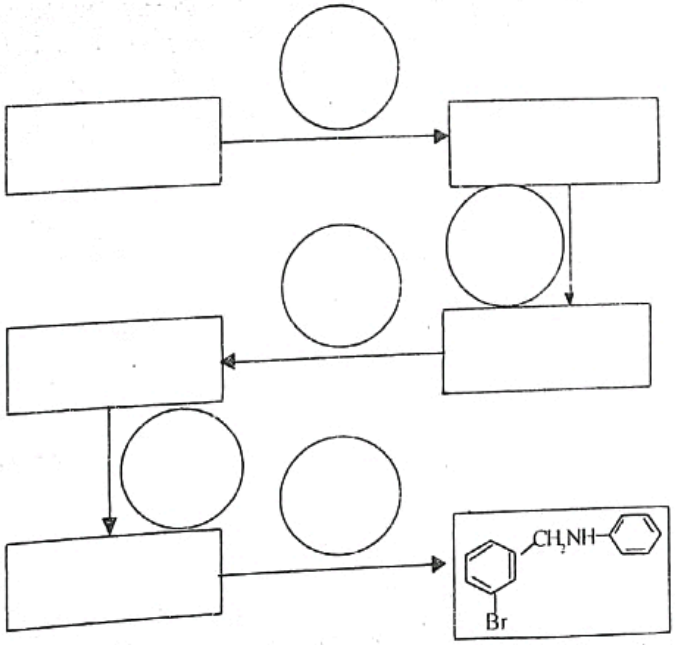


(4.9 marks)

(b) Show how you would synthesise the compound.



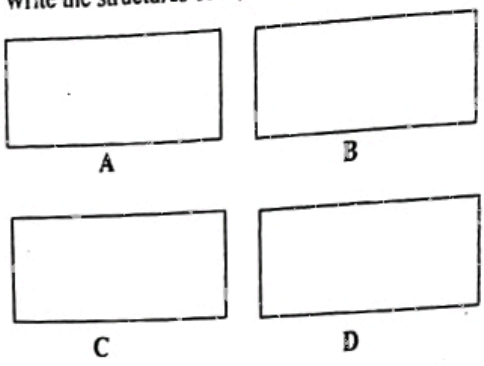
by completing the scheme given below.



(5.1 marks)

4. (a) A and B are isomeric hydrocarbons each having [illegible] hybridised carbon atoms and two sp^3 hybridised carbon atoms. Substitution of one of the hydrogen atoms in B by a chlorine atom gives C which shows optical isomerism. A and B separately react with a mixture of water, mineral acid and catalyst Y to give compound D. D has three sp^3 - hybridised carbon atoms. one sp^2 - hybridised carbon atom and one oxygen atom.

(i) Write the structures of A, B, C and D.



(ii) What is catalyst Y?

Y = ...

(iii) How would you distinguish between A and B using a chemical test?

(4.0 marks)

(b) Consider the reactions given in column P of the table below.

(i) Write the structure of the major organic product of each of the reactions in the respective cage in column Q of the table.

(ii) Identify the mechanism type of each of the reactions as

electrophilic addition (A_E),
electrophilic substitution (S_E)
nucleophilic addition (A_N)
nucleophilic substitution (S_N)
Elimination (E) or
any other mechanism (M_O)

by writing A_E, S_E, A_N, S_N, E or M_O in the appropriate cages in column R of the table.

(iii) In electrophilic reactions write the electrophiles in the appropriate cages in column S of the table.

(iv) In nucleophilic reactions write the nucleophiles in the appropriate cages in column T of the table.

(v) In each of the reactions wirte the colour of the main organic product in the appropriate cage in column U of the table

P	Q	R	S	T	U
Reaction	Major organic product	Mecha-nism type	Electrophile	Nucleo-phile	Colour
$CH_3CH_2CH_2I \xrightarrow{aq.NaOH}$					
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}=CH_2 \xrightarrow{dil.H_2SO_4}$					
$CH_3CH_2\underset{CH_3}{CHI} \xrightarrow[KOH]{alcoholic}$					
$C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl}$					
$CHO, NO_2 \xrightarrow{O_2N-C_6H_3-NHNH_2}$					
$CH_3, OH \xrightarrow{C_6H_5-N_2^+Cl^-}$					

(6.0 marks)

PART B - ESSAY

Answer two questions only. (Each question carries 15 marks.)

5. (a) Yeast cells obtain their energy requirements by incomplete oxidation of glucose ($C_6H_{12}O_6$) to alcohol (C_2H_5OH) and CO_2, by a process known as fermentation. This process can be represented as follows

$$C_6H_{12}O_{6\,(aq)} \rightleftharpoons 2\,C_2H_5OH\,(aq) + 2\,CO_2\,(g)$$

The standard enthalpies of combustion at 25°C of glucose(s) and alcohol(1) are -2808 kJ mol^{-1} and -1368 kJ mol^{-1} respectively.

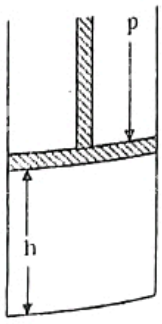
(i) Assuming that the enthalpy changes associated with the dissolution of glucose(s) and alcohol(l) in water are negligible, calculate the amount of energy released when 2.5 mol of glucose is fermented by yeast at 25°C.

(ii) What is the ratio between the energy released by fermentation of a certain amount of glucose and the energy released during 'respiration' of the same amount of glucose in man?

Note : In 'respiration' glucose is oxidised completely.

(4.0 marks)

(b) The figure alongside shows a rigid cylindrical vessel fitted with a weightless, frictionless and gas tight piston. 'h' is the height of the piston above the bottom of the vessel when the vessel contains a gas and 'p' is the external pressure acting on the piston. The area of cross section of the piston is 8.314 x 10^{-2} m^2.



(i) The vessel is initially filled with a gas X. When the temperature of the vessel and contents is 27°C and p is 10^5 Pa, h is 3.0 m. Calculate the number of moles of X in the vessel.

(ii) X dissociates when heated above 80°C, resulting in the following equilibrium.

$$2X(g) \rightleftharpoons Y(g) + Z(g)$$

The vessel in (i) above is heated and the contents allowed to reach equilibrium at 127°C keeping p constant at 10^5 Pa. Under these conditions, the vessel is found to contain 4.0 mol of X. Calculate the following :

(A) the value of h

(B) the partial pressures of the gases X, Y and Z.

(C) the equilibrium constant, K_p, for the above equilirium at 127°C.

(iii) 10.0 mol of an inert gas S is then introduced to the vessel in (ii) above and the system allowed to reach equilibrium at 127°C, keeping h at the same value as in (ii) (A) above. Calculate the values of partial pressures of X, Y, Z and S, and the value of p under these conditions.

(iv) p is then allowed to change back to 10s Pa, keeping the temperature of the mixture in (iii) above at 127°C. Calculate h, and the partial prssures of the gases X, Y, Z and S under the new equilibrium conditions.

(v) State any assumptions you made in these calculations.

(11.0 marks)

6. (a) Molecular iodine (I_2) can be partitioned between chloroform ($CHCl_3$) and water.

15.00 cm^3 of a 0.050 mol dm^{-3} solution of I_2 (in $CHCl_3$) is shaken well with 100.0 cm^3 of water and the system is allowed to attain equilibrium at 25°C. 5.00 cm^3 of the equilibrium $CHCl_3$ layer requires 24.00 cm^3 of a 0.020 mol dm^{-3} aqueous solution of $Na_2S_2O_3$ for complete reaction with the I_2 dissolved in the chloroform.

Calculate following :

(i) The concentrations of I_2 in the $CHCl_3$ and aqueous layers.

(ii) The partition coefficient for the partitioning of I_2 between $CHCl_3$ and water at 25°C.

(4.0 marks)

(b) I_2 also dissolves in aqueous KI solution to give the following equilibrium.

$$I_2(aq) + I^-_{(aq)} \rightleftharpoons I_3^-(aq)$$

$I_3^-(aq)$ and $I^-(aq)$ are not soluble in $CHCl_3$. Given below is an experimental procedure to determine the equilibrium constant, K_c, of the above equilibrium at 25°C.

The experiment in (a) above is repeated using 100.0 cm^3 of a 0.050 mol dm^{-3} aqueous solution of KI instead of the 100.0 cm^3 of water. 5.00 cm^3 of the $CHCl_3$ layer requires 8.00 cm^3 of 0.020 mol dm^{-3} aqueous $Na_2S_2O_3$ for complete reaction with the I_2 dissolved in $CHCl_3$.

Calculate the following :

(i) The concentrations of I_2 in the $CHCl_3$ and aqueous layers.

(ii) The number of moles of I_2 that reacted with $I^-(aq)$ to give $I_3^-(aq)$

(iii) The concentrations of $I^-(aq)$ and $I_3^-(aq)$

(iv) The equilibrium constant, K_c, at 25°C for the $I_2(aq)$, $I^-(aq)$ and $I_3^-(aq)$ equilibrium.

(10.0 marks)

(c) 'Tincture of Iodine' is a solution of I_2 in aqueous KI, used for the disinfection of wounds. Give two reasons for the use of this solution, rather than an aqueous solution of I_2 for the above purpose.

(1.0 marks)

7. (a) (i) A 100 cm^3 of 0. 100 mol dm^{-3} aqueous $CuSO_4$ solution containing a small amount of Na_2SO_4 was electrolysed using two clean copper (Cu) electrodes, each with a mass of 10.0 g. During this experiment, a current of 300 mA was passed for 9.65 minutes.
Calculate
(A) the mass of the cathode
(B) the mass of the anode, and
(C) the concentration of Cu^{2+} ions in the solution at the end of this electrolysis experiment.

Note : Charge of 1 mol of electrons is 96500 C. Cu = 63.5

(ii) At the end of the experiment described in (i) above, 100 cm^3 of water was added to the electrolyte solution, the solution was stirred, and the electrolysis was continued by passing a current of 300 mA for a further 9.65 minutes.
Deduce
(A) the mass of the cathode
(B) the mass of the anode, and
(C) the concentration of Cu^{2+} ions in the solution at the end of this electrolysis experiment.

(iii) Is electrolysis a good method to discharge only Pb^{2+} ions from a solution containing both Pb^{2+} and Cu^{2+} ions? Give reasons for your answer.
$E^0_{Cu^{2+}(aq)/Cu(s)} = 0.34$ V ; $E^0_{Pb^{2+}(aq)/Pb(s)} = -0.13$ V

(5.0 marks)

(b) An aqueous solution contains Na_3PO_4 and Na_2SO_4 only. Excess of aqueous $Ba(OH)_2$ solution is added to this solution with stirring until no further precipitation is observed.
In this experiment, it was found that 200 cm^3 of 5.0×10^{-3} mol dm^{-3} $Ba(OH)_2$ solution has been added for 100 cm^3 of the above solution. When the precipitate was filtered, washed and dried, its weight was found to be 0.1435 g. The concentration of SO_4^{2-} (aq) in the filtrate was found to be 1.1×10^{-7} mol dm^{-3}.

(i) Calculate the concentration of Ba^{2+} in the filtrate.

(ii) Hence calculate the number of moles of Ba^{2+} in the precipitate.

(iii) Hence calculate the number of moles of $BaSO_4$ and the number of moles of $Ba_3(PO_4)_2$ in the precipitate.

(iv) Hence calculate the concentrations of PO_4^{3-} and SO_4^{2-} in the initial solution.
(O = 16.0, Na = 23.0, P = 31.0, S = 32.0, Ba = 137.0)

Solubility product of $BaSO_4$ at 25°C = 1.1×10^{-10} mol^2 dm^{-6}

Solubility product of $Ba_3(PO_4)_2$ at 25°C
$= 3.4 \times 10^{-23}$ mol^5 dm^{-15}

(10.0 marks)

PART B - ESSAY

Answer two questions only. (Each question carries 15 marks.)

8. (a) L and M are 3d transition elements.
L forms an oxyanion which is tetrahedral in shape
M forms a cation M^{2+}
One mole of the oxyanion of L reacts with five moles of M^{2+}, oxidising it to M^{3+} and forming L^{2+}.
An aqueous solution of M^{3+} is yellow-brown in colour and liberates I_2 from KI.

(i) Deduce the oxidation state of L in the oxyanion.

(ii) What are the elements L and M?

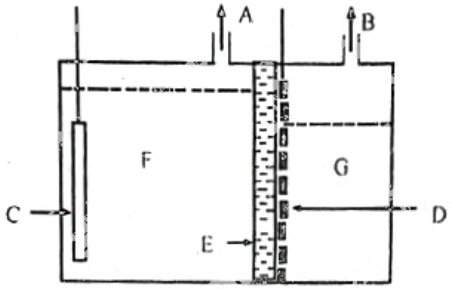
(iii) Write the chemical formula of the oxyanion of L.

(iv) Give the reducing agents and the reaction conditions employed in a method used industrially to convert M_2O_3 to the element M.

(v) Give one reaction of $L(OH)_2$ useful in quantitative analysis.

(7.5 marks)

(b) A diagram of the diaphragm cell used to manufacture NaOH is given below.



(i) Name A, B, C, D and E.

(ii) What are the constituents of solutions F and G?

(iii) Indicate the materials used for the anode and cathode?

(iv) What factors must be taken into consideration in selecting materials for the anode and the cathode?

(v) What is the role of the diaphragm?

(vi) Explain why the solution level of one compartment is usually maintained at a higher level than that of the other compartment.

(vii) Give two reasons for the use of brine but not a dilute solution of NaCl as the electrolyte.

(7.5 marks)

9. (a) Tests carried out with a salt X and the relevant observations are given below.

Test	Observations
(A) Warmed X with dil HCl	Colurless solution. No evolution of gases.
(B) Passed H_2S through solution in (A) above.	Orange coloured precipitate.
(C) Diluted a solution of X in dil. HCl, with water.	A white precipitate
(D) Warmed X with NaOH solution.	No gas evolved.
(E) Warmed X with NaOH solution and Al powder.	Ammonia evolved.

(i) State the inferences that you can make from each of the above tests.

(ii) Identity the salt X.

(iii) Give one test to confirm the identity of the anion.

(5.0 marks)

(b) (i) A solution B contains SO_3^{2-} and $C_2O_4^{2-}$ ions. 25.0 cm^3 of solution B required 40.0 cm^3 of 0.05 mol dm^{-3} $KMnO_4$ solution for complete reaction under acidic conditions. The resulting solution was treated with excess of $BaCl_2$ in the presence of dil. HNO_3. The mass of the white precipitate so obtained after drying was 0.466 g.

Calculate the concentrations of SO_3^{2-} nad $C_2O_4^{2-}$ ions in solution B.

(Ba = 137.0 : S = 32.0 O = 16)

(ii) You are provided with a finely powdered mixture containing Fe, Al, Cu and Zn. using **only** the chemicals given below, briefly indicate a chemical method (no experimental details required) to determine the mass percentage of each metal in the mixture.

Chemicals : dilute H_2SO_4, aqueous NaOH, and dilute NH_4OH

(10.0 marks)

10. (a) (i) Write structures of (A) P_4 (white phosphorus) molecule and (B) three (noncyclic) oxyacids of phosphorus.

Write the names of these three oxyacids and indicate the oxidation number of the phosphorus atom in each case.

(ii) White phosphorus(P_4) reacts with $Ba(OH)_2$ solution forming barium hypophosphite and a gaseous product containing phosphorus.

Write a **balanced** chemical equation for this reaction.

Indicate the oxidation number of each phosphorus atom in the reactant and the products.

Based on these oxidation numbers, name the type of this reaction.

(iii) Nitrogen exists as N_2 molecules with a N ≡ N bond while phosphorus exists as P_4 molecules with P-P bonds.

Explain this using the following bond dissociation energies (kJ mol^{-1})

(N ≡ N 946 : P ≡ P 490 . N - N 160 ; P - P 200)

10.0 marks

(b) A mixture contains $CaCO_3$, $MgCO_3$ and SiO_2 only. The molar ratio of $CaCO_3$: $MgCO_3$ = 1 : 1 ..... 2.00 g of this mixture was heated strongly to a constant mass, the mass of the residue obtained 1.12 g. Calculate the mass percentage of each component in the mixture.

(Ca = 40. 0 ; Mg = 24 . 0; Si = 28. O : 0 = 16. O)

(5.0 marks)

The Periodic Table

1	1 H																2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun	111 Uuu	112 Uub	113 Uut	....				

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr