PART A — STRUCTURED ESSAY

Answer all four questions. Each question carries 16 marks.

1. (*a*) Q and R are two non-transition elements in the same group belonging to two consecutive periods of the periodic table. They form the compounds RQ_2 and RQ_3.

(i) Identify Q and R below:

Q = ... ; R = ...

(ii) Indicate below all the stable oxidation states shown by **Q** and **R**.

Indicate also the chemical formula of an illustrative compound for **each** such stable oxidation state of **each** element.

(N.B.:– Against each such chemical formula, the oxidation state of the relevant element must also be correctly given.)

Q : .....

.....

.....

R : .....

.....

.....

(4.0 marks)

(*b*) Draw in the relevant boxes below the dot and cross diagrams of the molecules N_2O_4 and O_3 indicating valence electrons of all atoms.

(i) N_2O_4	(ii) O_3

(3·0 marks)

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(c) A, B and C are experimental observations. Given against each of them are some explanations provided by students for these observations. Of these explanations given for each observation, **one or more** may be correct.

Evaluate these explanations by

(i) marking in the appropriate box a ☑ if, in your opinion, the explanation is **valid**.

(ii) marking in the appropriate box a ☒ if, in your opinion, the explanation is **invalid**.

Keep the appropriate box empty as ☐ if you are **unable** to evaluate the validity of the explanation.

N.B. : For every correct answer, 0·3 marks each will be awarded.
For every incorrect answer, 0·2 marks each will be deducted.
If a box is kept empty, no marks will be awarded or deducted.
However, the minimum marks for this part (c) will be zero (0).

Experimental Observation	Students' Explanation
A- When a beam of α-particles falls on a thin gold plate, most of the α-particles pass undeflected through the plate.	☐ The gold plate contains spaces which are large compared with the size of α-particles. ☐ The gold plate is non-continuous. ☐ The path of α-particles is always linear.
B- A paddle wheel placed in the path of cathode rays rotates.	☐ Cathode rays are negatively charged. ☐ Cathode rays have particle-like properties. ☐ Material of the paddle wheel is continuous.
C- The electronic emission spectrum of hydrogen consists of several series of lines; in each series, the separation between the lines decreases as the frequency increases.	☐ There are definite energy levels for the electrons in the H-atom. ☐ The energy corresponding to each line in the spectrum is equal to the energy of an electronic level of hydrogen. ☐ The energy of the electron decreases with increasing radius of the atomic shell. ☐ The energy difference between successive levels decreases as the energy of the electronic levels increases.

(3·0 marks)

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2. (*a*) On complete thermal decomposition in an inert environment, an inorganic salt **X** gave 1·52 g of Cr_2O_3, 0·72 g of H_2O and 0·28 g of N_2 as the only products.
(Relative atomic masses : H = 1; N = 14; O = 16; Cr = 52)

(i) Deduce the empirical formula of **X**.

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(ii) One mole of **X** contains two moles of Cr. Compound **X** does not contain H_2O molecules. Identify below the cation and anion present in **X**.

cation : .....; anion : .....

(iii) Write below the chemical formula of **X**.

.....

(3.0 marks)

(*b*) (i) **Z** is a metallic element.

Oxalate $\left(C_2O_4^{2-}\right)$ ions are converted to CO_2 by ZO_4^- ions in an acidic medium.

ZO_4^- ions are converted to ZO^+ ions during this reaction.

Write below the relevant **balanced** ionic half reactions.

.....

.....

(ii) Write below the stoichiometry of the above reaction between $C_2O_4^{2-}$ and ZO_4^- ions.

$C_2O_4^{2-}$: ZO_4^- = ... : .....

(2.0 marks)

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(c) Complete the passage below correctly by filling each of the 26 blank spaces with the most appropriate word. **(N.B. : Each blank space should be filled with <u>one word</u> only.)**

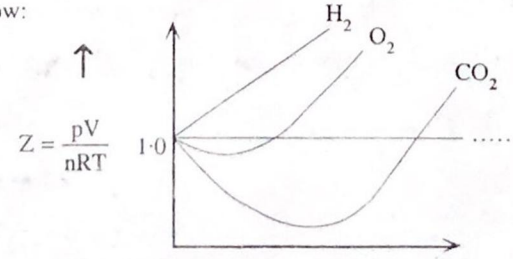
THE BEHAVIOUR OF MATTER

Solids, liquids and gases are commonly referred to as the three ..... of matter. There is very little free space in between the particles / molecules constituting solids and liquids. At a given temperature, solids and liquids, relative to gases, therefore have a definite ..... and a high ..... . These two physical properties are hardly affected by (small) changes in pressure and temperature. Solids differ from liquids and gases by the presence of a definite .....; constituent particles of a solid are also able to ..... about mean positions.

According to the molecular kinetic theory of gases, gaseous molecules are in constant ..... motion during which .... collisions occur. Gases that behave in this manner are referred to as ideal gases. Characteristic properties of ideal gases are the absence of ..... between molecules and the absence of ..... volumes. At a constant temperature, the total ..... of the system must remain unaltered; speeds of such gas molecules can vary from approximately ..... to very ..... values. The variation of the distribution of molecular speeds of an ideal gas with molar mass and ..... can be explained by means of a mathematical equation put forward in 1860 and commonly known as the Maxwell – Boltzmann distribution of molecular speeds.

The pressure, p, of an ideal gas can be calculated using the expression $3pV = mN\overline{c^2}$ where m is the mass of one ..... and N is the number of ..... . At a given temperature, the pressure of the gas does not vary with ..... . Therefore the ..... speed of molecules must remain unchanged with time at a given temperature. Although this speed ..... with temperature, it is incorrect to say that the speeds of **all** molecules in the system are simultaneously ..... as a result of an increase of temperature.

.... gases do not usually behave as ideal gases. The behaviour of such gases approximates to the behaviour of ideal gases at low ..... and .... Deviation of non-ideal gases from ideal gas behaviour can be depicted by a plot of compressibility factor (Z) against ..... as shown below:



..... gas

(5·0 marks)

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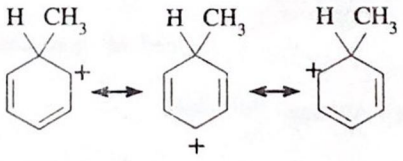
3. (*a*) A compound X of molecular formula $C_8H_{18}O_6$ contains hydroxyl groups. When **X** is reacted with excess ethanoyl chloride, the product obtained has a relative molecular mass of 378. Calculate the number of hydroxyl groups in **X**.
(Relative atomic masses : C = 12; H = 1; O = 16; Cl = 35·5) *(2.5 marks)*

(*b*) Three isomeric amines **A**, **B** and **C** (molecular formula $C_4H_{11}N$) on reaction with $NaNO_2/HCl$ produces three alcohols **D**, **E** and **F** (molecular formula $C_4H_{10}O$) respectively. Although **D** reacts quickly with Lucas reagent, **E** and **F** do not react with Lucas reagent at room temperature. **D** is not easily oxidized. **E** and **F** can be oxidized to **G** and **H** respectively. Both **G** and **H** form precipitates with Brady's reagent and also reduces Fehling's reagent. Write possible structures **(see instruction box in page 1)** for **A**, **B**, **C**, **G** and **H** in the relevant boxes below.
(2.5 marks)

A	B	C

G	H

(*c*) (i) The intermediate represented by the resonance structures,



occurs in a reaction leading to the synthesis of toluene.

(I) Write the reactants and reagents that give this intermediate.

.....

(II) Write below a mechanism to explain the formation of the intermediate. *(3.0 marks)*

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(ii) Methyl chloride is formed as a major product, when equimolar amounts of CH_4 and Cl_2 are reacted in the presence of light.

(I) Write **two** steps in the mechanism of the above reaction in which methyl chloride is a product. (Methyl chloride should be a product in **each** of these two steps.) Indicate electron movements. *(1.0 mark)*

.....

.....

(II) Ethane is also formed but only in a **very small** quantity in the above reaction. Explain this. *(1·0 mark)*

.....

.....

.....

.....

.....

4. *(a)* (i) A saturated non cyclic hydrocarbon, C_nH_m, has one asymmetric centre. Write the smallest possible numbers for n and m.

n = ... ; m = ...

(ii) Write the structures (see **instruction box in page 1**) of the structural isomers of this hydrocarbon. *(2·5 marks)*

(b) (i) Without the use of catalytic hydrogenation, show how you would convert $CH_3CH_2C{\equiv}CH \longrightarrow CH_3CH_2CH_2CH_3$ utilising **not more than three** steps.

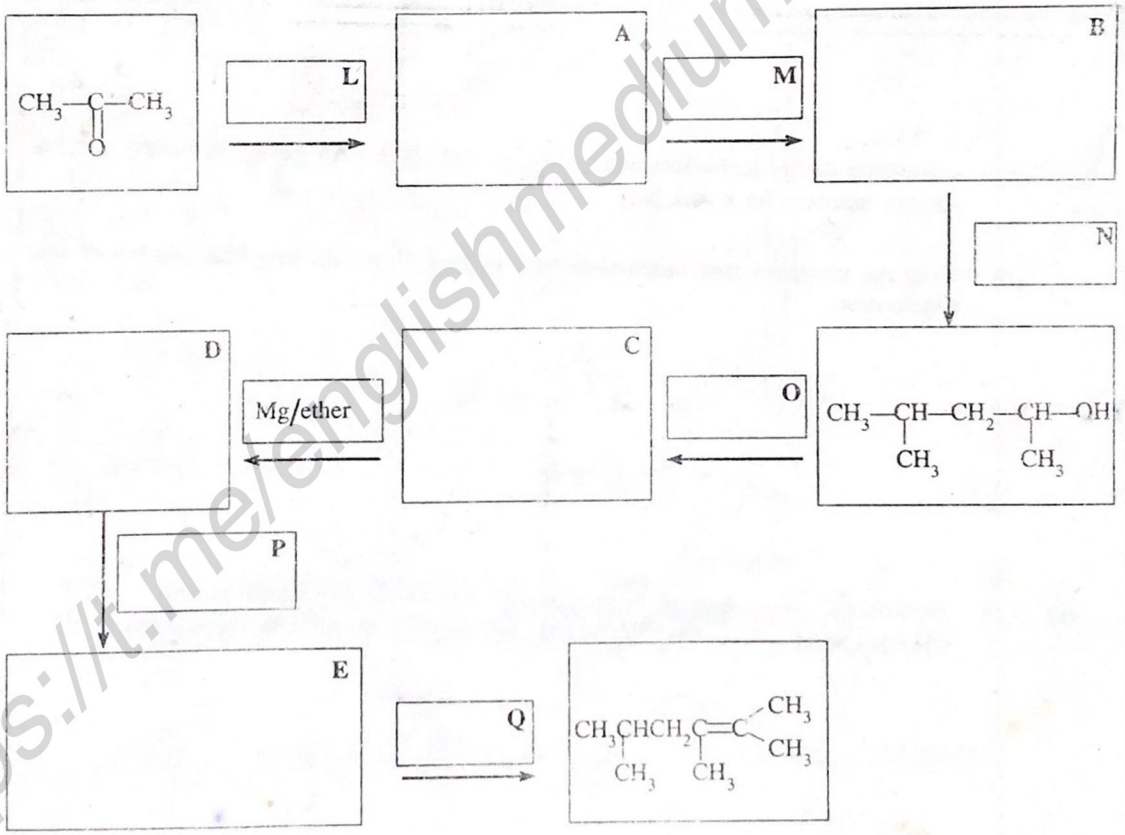
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(ii) Without the use of CN^- ion as a reactant, show how you would convert

$CH_3CH_2CH_2OH \longrightarrow CH_3CH_2CN$ utilising **not more than five** steps. *(2·5 marks)*

(*c*) Consider the reaction scheme represented through the boxes below :–



(i) Write the structures (see instruction box in page 1) of the compounds corresponding to A, B, C, D and E in the relevant boxes.

(ii) Write the reagents corresponding to L, M, N, O, P and Q. Amongst these reagents the only organic compound allowed is 2–propanone.

(5·0 marks)

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முழுப் பதிப்புரிமையுடையது)
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ශ්‍රී ලංකා විභාග දෙපාර්තමේන්තුව / இலங்கைப் பரீட்சைத் திணைக்களம் / Department of Examinations, Sri Lanka

අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2001 අගෝස්තු
கல்விப் பொதுத் தராதரப்பத்திர(உயர் தர)ப் பரீட்சை, 2001 ஒகஸ்ற்
General Certificate of Education (Adv. Level) Examination, August 2001

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

02
E | II

PART B — ESSAY

Answer two questions only. Each question carries 15 marks.

5. (*a*) Standard molar enthalpies of neutralisation (ΔH°) obtained at 25°C for some acids with NaOH in aqueous solution, are given below:

acid	ΔH°/ kJ mol^{-1}
HCl	– 57
HNO_3	– 57
C_2H_5COOH	– 51

(i) Provide reasons for the above observations.

(ii) Deduce the standard molar enthalpy of dissociation (ΔH°) at 25°C of

(I) water

(II) propanoic acid (C_2H_5COOH) in water.

(4.0 marks)

(*b*) The following data are provided :–

heat source	relative molecular mass	standard boiling point/°C	standard molar enthalpy of combustion, ΔH°/kJ mol^{-1}
$C_3H_8(g)$	44	– 42	– 2,200
$C_8H_{18}(l)$	114	+ 126	– 5,130

(i) Under standard conditions, 1·0 kg each of propane and octane is separately subjected to complete combustion. Calculate, in each case

(I) the heat energy that is evolved.

(II) the mass of gaseous CO_2 that is produced.

(ii) Using your results from (i) above, deduce, giving **two** reasons, which of the two compounds would be more advantageous as a heat source.

(5·0 marks)

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(c) An insecticide **X** is soluble in chloroform as well as in water. By shaking an aqueous solution of **X** with chloroform, some of the **X** can be extracted into the chloroform layer.

1·0 dm^3 of an aqueous solution of 0·18 mol dm^{-3} **X** was extracted with a total volume of 1·0 dm^3 of chloroform at 25°C. **Two** alternate extraction procedures (**p**) and (**q**) described below were used for this purpose :–

(**p**) Extraction with 1·0 dm^3 of chloroform in one step : here the chloroform layer is found to contain 0·144 mol **X**.

(**q**) Extraction with two successive 500·0 cm^3 portions of chloroform in two steps.

(i) Write down an expression for the partition coefficient, K, for **X** between chloroform and water.

(ii) Calculate the value of K at 25°C.

(iii) Hence, calculate the total number of moles of **X** extracted in the two 500·0 cm^3 portions of chloroform in procedure (**q**).

(iv) Deduce which of the two extraction procedures, (**p**) or (**q**), is more efficient for the extraction of **X** from an aqueous solution into chloroform.

(v) The molar enthalpy of solution of **X** in water and chloroform are $-2{\cdot}5$ kJ mol^{-1} and $-1{\cdot}5$ kJ mol^{-1} respectively.
Using this data, show, with reasons, how you would change the temperature, to make the extraction more efficient.

(6.0 marks)

6. (*a*) A glass vessel of volume 5·0 dm^3 is filled with a gaseous compound **P**, which behaves ideally. At 27°C, the pressure of the gas inside the vessel is $1{\cdot}995 \times 10^5$ N m^{-2}.

At temperatures above 100°C, **P** dissociates yielding the following equilibrium :–

$$\mathbf{P}(g) \rightleftharpoons \mathbf{Q}(g) + \mathbf{R}(g)$$

When the vessel containing **P** at 27°C is heated to 127°C, the pressure inside the vessel reaches a constant value of $4{\cdot}656 \times 10^5$ N m^{-2}. The volume of the vessel is unchanged on heating.

(i) Calculate to the nearest first decimal place, the total number of moles of gas present in the vessel under each of the following conditions :–
(I) at 27°C
(II) when equilibrium is reached at 127°C.

(ii) Hence calculate the equilibrium constant, K_p, for the above equilibrium at 127°C.

(iii) An **inert** gas **Z** is then introduced into the vessel.
When the system thereafter reaches equilibrium again at 127°C, the pressure inside the vessel is found to be $6{\cdot}651 \times 10^5$ N m^{-2}.
Obtain the partial pressures and mole fractions of **P**,**Q**, **R** and **Z** under these conditions.

N.B. : State the assumptions, if any, you make.

(7.5 marks)

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(b) Two volatile liquids **A** and **B** form ideal solutions with each other at all compositions. One such solution begins to boil at a temperature of 68°C under an external pressure of 1 standard atmosphere.

The mole fraction of **A** in the liquid phase of this boiling solution is 0·76 while the mole fraction of **B** in the vapour phase of the same solution is 0·18.

The saturated vapour pressure of pure **A** is greater than that of pure **B** at all temperatures.

At 68°C, the saturated vapour pressures of pure **A** and pure **B** are P_A^0 and P_B^0 respectively.

1 standard atmosphere can be taken as $1{\cdot}0 \times 10^5 \text{ N m}^{-2}$.

(i) Explain the ideal behaviour of a binary mixture of **A** and **B** in terms of inter-molecular interactions.

(ii) Calculate (in units of pascal) the vapour pressures P_A and P_B of **A** and **B** respectively in the above mentioned solution boiling at 68°C. State the assumption that you make.

(iii) Write down the mathematical relationship between P_A and P_A^0 at 68°C.

(iv) State, giving reasons, which of the pure liquids (**A** or **B**) will have a standard boiling point higher than 68°C.

(v) Sketch the temperature vs composition diagram for the **A/B** system under an external pressure of one standard atmosphere and label it fully.

(vi) Mark clearly the following on the above diagram :
(I) the temperature 68°C
(II) the compositions of the liquid and vapour phases in equilibrium at 68°C.

(vii) If the boiling of the liquid is continued, state what changes you would expect in
(I) the mole fraction of **A** in the liquid.
(II) the boiling point of the liquid.
Give reasons for your answers. *(7.5 marks)*

7. (*a*) **L** and **M** are two metals which form only divalent cations. At a temperature of 25°C, a piece of **L** was placed in an aqueous solution of MSO_4. Deposition / precipitation of the metal **M** and dissolution of the metal **L** in the solution were observed.

The standard electrode potential (E°) of one of these two metals is –1·23 V and that of the other metal is –2·12 V at 25°C.

(i) Write the equation for the chemical reaction consistent with the above observations.

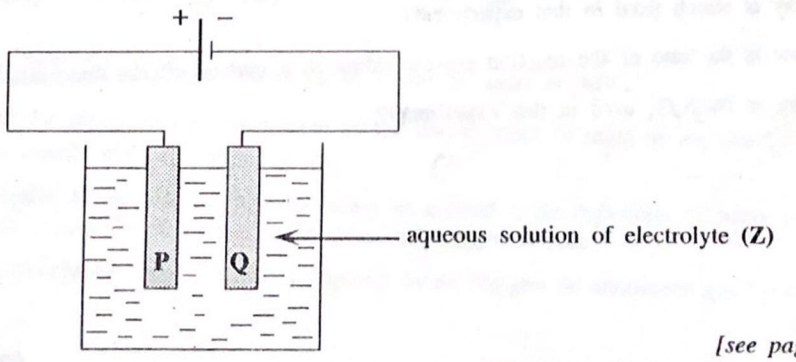
(ii) Write the oxidation and reduction half reactions relevant to the chemical reaction corresponding to (i) mentioned above.

(iii) The reaction in (i) above is the nett cell reaction that occurs during the discharge of an electrochemical cell. Using standard notation, write down the electrochemical cell considering it to be in its standard state.

(iv) Calculate the electromotive force (e.m.f.) at 25°C of the electrochemical cell mentioned in (iii) above.

(3·5 marks)

(*b*) The following type of electrical circuit (with electrodes **P** and **Q**) was used in an electrolytic method to deposit a layer of pure Cu metal on a rod of carbon. Neither **P** nor **Q** is Cu.



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(i) Identify on which of the **two** electrodes (**P** or **Q**), Cu will be deposited, stating also whether it is the anode or cathode.

(ii) Suggest a suitable electrolyte that can be used as **Z**.

(iii) Write down the ionic half-reaction that initially takes place at the cathode.

(2·5 marks)

(*c*) At 25°C, an aqueous solution of 0·1 mol dm^{-3} $AgNO_3$ is slowly added into an aqueous solution which is 0·01 mol dm^{-3} with respect to the salt NaX and 0·01 mol dm^{-3} with respect to the salt NaY.

Here, X^- and Y^- are two halide ions.

The solubility products of the two silver halides in water at 25°C are given below :–

AgX : 1×10^{-10} mol^2 dm^{-6}

AgY : 1×10^{-18} mol^2 dm^{-6}

(i) Deduce whether AgX or AgY will be precipitated first.

(ii) At the instant when the second silver halide just begins to precipitate, calculate the remaining concentration of the halide ion which was precipitated first.

(iii) State the assumption that is essential to carry out the above calculations.

(4.5 marks)

(*d*) In an experiment where the effect of $Fe^{3+}(aq)$ concentration on the rate of the reaction

$$2\ Fe^{3+}(aq) + 2\ I^-(aq) \longrightarrow 2\ Fe^{2+}(aq) + I_2(aq)$$

is studied, reaction mixtures are prepared by mixing reagents as given in the following table :–

Experiment No.	Boiling Tube A		Boiling Tube B	
	Water/cm^3	0·1 mol dm^{-3} Fe(III) solution/cm^3	1·0 mol dm^{-3} KI solution/cm^3	0·0005 mol dm^{-3} $Na_2S_2O_3$ solution containing starch/cm^3
1	–	25·0	10·0	15·0
2	5·0	20·0	10·0	15·0
3	10·0	15·0	10·0	15·0
4	15·0	10·0	10·0	15·0
5	20·0	5·0	10·0	15·0

(i) Why is starch used in this experiment?

(ii) How is the rate of the reaction corresponding to a given $Fe^{3+}(aq)$ concentration measured?

(iii) Why is $Na_2S_2O_3$ used in this experiment?

(4.5 marks)

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PART C — ESSAY

Answer two questions only. Each question carries 15 marks.

8. (*a*) M is a first row *d* block element. It shows the highest stable oxidation state in MO_4^-.

(i) Write the **complete** electronic configuration of M.

(ii) Identify M.

(iii) Write the **stable lowest** oxidation state of M in an aqueous solution.

(iv) Write the reagents required to convert MO_4^- to a species with the oxidation state given by you in (iii).

(v) Write **one** important use of M.

(3·6 marks)

(*b*) Write the products formed when each of the following compounds reacts with H_2O :

(i) CaC_2 (ii) Mg_3N_2 (iii) $BiCl_3$ (iv) AlH_3

(2·4 marks)

(*c*) An aqueous solution contains Al^{3+}, Zn^{2+} and Mg^{2+} as the only metal ions.

Using solutions of NH_4OH, NH_4Cl, NaOH and dilute HCl only, how would you show the presence of each of these metal ions in the above solution?

(3·0 marks)

(*d*) When 0·92 g of a finely powdered mixture containing $CaCO_3$ and $MgCO_3$ was heated to a high temperature, 0·48 g of a mixture containing CaO and MgO only was obtained.
Calculate the mass percentage of $CaCO_3$ in the original mixture.

(Relative atomic masses : C = 12; O = 16; Mg = 24; Ca = 40)

(3·0 marks)

(*e*) Deduce the shape of each of the following species and name these shapes.

(i) PCl_4^+ (ii) PCl_5 (iii) PCl_6^- *(3·0 marks)*

9. (*a*) (i) Write names and the corresponding chemical formulae of the allotropic forms of the element oxygen.

(ii) Write **balanced** chemical equations for all the possible reactions that can occur when each of the following elements is burnt in an equimolar gaseous mixture of oxygen and nitrogen.
(I) K (II) Mg (III) Al

(iii) State whether each of the following oxides is acidic, basic or amphoteric.
(N.B. : 0·2 marks will be awarded for each correct answer;
0·1 marks will be deducted for each incorrect answer;
However the minimum mark for this part (iii) will be zero.)

(I) CaO (II) BaO (III) P_2O_5
(IV) Bi_2O_3 (V) SO_2 (VI) NO_2

(5·7 marks)

(*b*) There is $2·0 \times 10^{-4}$ mol of oxygen dissolved in 1 dm^3 of water at 30°C.

(i) Calculate the dissolved oxygen content of the above water in units of mg dm^{-3}.
(Relative atomic mass of oxygen = 16)

(ii) The depletion of dissolved oxygen of water in a pond is an indication of water pollution.
Write **one** reason for the depletion of dissolved oxygen in water.

(iii) Chlorine gas can be used to disinfect drinking water. Suggest an alternative gas for this purpose.

(3·0 marks)

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(*c*) A 200·0 cm^3 portion of a water sample was reacted with excess manganese(II) sulphate and alkaline KI. After shaking, it was kept for 10 minutes and then acidified. The liberated I_2 was titrated with 0·01 mol dm^{-3} solution of $Na_2S_2O_3$.

(i) Write **balanced** chemical equations for the reactions which occur in the above procedure.

(ii) Calculate the dissolved oxygen in the water sample in units of mg dm^{-3} if the volume of 0·01 mol dm^{-3} $Na_2S_2O_3$ consumed in the titration was 20·0 cm^3.
(Relative atomic mass of oxygen = 16)

(iii) State **two** important steps you should take to minimize errors in the above procedure for determining dissolved oxygen.

(6·3 marks)

10. (*a*) (i) Describing the necessary conditions clearly and using **balanced** chemical equations, state the essential steps involved in the manufacture of nitric acid by Ostwald method.

(ii) State **two** possible harmful effects of each of the gaseous products formed during the process referred to in (i), if leaked accidentally to the environment. (Details not required).

(iii) State **briefly three** ways in which nitric acid can harm the environment if leaked accidentally to a lake.

(8·0 marks)

(*b*) A commercial fertilizer sample contains urea and ammonium nitrate.

In a laboratory experiment, 0·16 g of this sample was heated with excess 4·0 mol dm^{-3} NaOH in a flask. The liberated gas was absorbed in 50·0 cm^3 of 0·1 mol dm^{-3} HCl. The remaining HCl was back titrated with 0·1 mol dm^{-3} NaOH. The volume of 0·1 mol dm^{-3} NaOH required for this titration was 25·0 cm^3.

The remainder of the solution in the flask was then heated with aluminium powder until bubbling stopped. Here, too, the gas liberated was absorbed in another 50·0 cm^3 of 0·1 mol dm^{-3} HCl; the remaining HCl was back titrated with 0·1 mol dm^{-3} NaOH. For this titration, the volume of 0·1 mol dm^{-3} NaOH required was 40·0 cm^3.

(i) Write down **balanced** chemical equations for **all** the reactions encountered above.

(ii) Using the above data, calculate the mass percentages of urea and ammonium nitrate present in the commercial fertilizer sample.
(Relative atomic masses : H = 1; C = 12; N = 14; O = 16)

(7·0 marks)

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